MIGRATION FROM NON-OVENABLE FOOD CONTACT MATERIALS AT ELEVATED TEMPERATURES

by

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STATEMENT

The work submitted in this thesis was carried out by the author in the School of Applied Sciences at De Montfort University, between November 1990 and October 1993. Unless otherwise accredited the work was carried out by the author and has not been submitted in any other form for any other degree or qualification.

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ABSTRACT

A major problem associated with the development of complex polymeric materials for food contact applications is the potential for migration of toxic substances from the polymer to the food. This thesis investigates the transfer of migrants from non-ovenable food contact materials at elevated temperatures, and several applications where migration has occurred have been identified. Boil in the bag applications lead to exposure times of 30 - 120 minutes for complex multilayer laminates, whilst plastic kettles are repeat exposure items, and plastic 'vacuum flasks' have a potential for up to 4 hours exposure.

Analytical techniques including, GC-MS, LC-MS, HPLC and UV spectroscopy have been employed to quantify the species migrating from these food contact materials into aqueous and oil simulants, and to ensure that they conform to the implemented EC restrictions. Olive oil is a stipulated EC fatty food simulant, but it is unsuitable for specific migration analyses since it contains many interfering compounds. These could not be eliminated by repeated solvent extraction, and a silicone oil was therefore substituted.

In an attempt to identify the species migrating into aqueous and fatty food simulants both the final materials and also the individual components i.e. nylon, adhesive, polyethylene and polypropylene were examined separately. HPLC techniques have been developed to quantify both the known levels of antioxidants present in the polymers and also the anticipated degradation products from these materials. Typical levels of antioxidants in simulants range from <0.1 (aqueous) to 45μg dm^{-2} (oil) and <0.1 (aqueous) to 200μg dm^{-2} (oil) for antioxidant degradation products.

In commercial boil in the bag laminates the major migrants have been shown to be derived principally from the nylon film, and the polyurethane adhesive used to fabricate the laminate. LC-MS investigations have confirmed the presence of the residual monomer ε-caprolactam and its cyclic oligomers (up to the nonamer) in aqueous food simulants boiled in direct contact with the nylon 6. This technique has also identified the main migrants from the aliphatic and aromatic polyurethane adhesives to be residual oligomers from the polyols. Any residual isocyanates in the adhesive are converted to the corresponding amine, and colourimetric assays have determined levels between 1.1 and 0.1μg dm^{-2}.

Measured, migration levels into fatty food simulants were found to be greater than in aqueous food simulants. However, none of the material examined showed an overall migration value greater than the EC limit of 10mg dm^{-2} for single sided testing. Some instances were found where the consumer was instructed to boil the dry food part of a boil in the bag meal in the same water as that used to heat the pouch containing the meat, and under these circumstances a total migration value for the laminate greater than 10mg dm^{-2} was measured.

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ABBREVIATIONS

2,4,6-TTBP	2,4,6-tri-tert-butylphenol
2,4-DTBP	2,4-di-tert-butylphenol
2,6-DTBBQ	2,6-di-tert-butyl-1,4-benzoquinone
2,6-DTBP	2,6-di-tert-butylphenol
3,5-DTBP	3,5-di-tert-butylphenol
ADI	acceptable daily intake
BHA	2,6-di-tert-butyl-4-methoxyphenol
BHT	2,6-di-tert-butyl-4-methylphenol
EI-MS	electron impact mass spectroscopy
FAB	fast atom bombardment
FDA	Food and Drugs Administration
GC	gas chromatography
GC-MS	gas chromatography - mass spectroscopy
GPC	gel permeation chromatography
HDI	hexamethylene diisocyanate
HDPE	high density polyethylene
HPLC	high performance liquid chromatography
IPDI	isophorone diisocyanate
IR	infra-red spectroscopy
Irgafos 168	tris (2,4-di-tert-butylphenyl) phosphite
Irgafos P-EPQ	tetrakis (2,4-di-tert-butylphenyl) 4,4'-biphenylenediphosphonite
Irganox 1010	pentaerythritol-tetrakis-[3,(3'-5'-di-tert-butyl-4-hydroxyphenyl) propionate]
Irganox 1076	octadecyl -3- (3',5' -di-tert-butyl-4'-hydroxyphenyl) propionate
Irganox 1330	1,3,5-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)-2,4,6-trimethylbenzene
LC-MS	liquid chromatography - mass spectrometry
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
MDA	4,4'-methylenedianiline
MDI	methylenebis (phenyl isocyanate)
MS	mass spectrometry
NEDD	N-(1-naphthyl) ethylene diamine dihydrochloride
NIOSH	National Institute for Occupational Safety and Health
NMR	nuclear magnetic resonance spectroscopy
PP	polyproylene
SCF	scientific comittee for food
SFC	supercritical fluid chromatography
SFE	supercritical fluid extraction
SML	specific migration limit
TDI	tolerable daily intake
TDTBPP	tris (2,4-di-tert-butyl-phenyl)phosphate [oxidised Irgafos 168]
TWA	time weighted average

CHAPTER 1 : INTRODUCTION

1.1 FOOD PACKAGING

The principal functions of food packaging are to protect the food contents from physical damage, losses, or deterioration, and to facilitate distribution from processor to consumer. Food packaging must also attractively identify the product and must perform these functions at minimum system cost because the package itself has no intrinsic value to the consumer. Food packaging assists product preservation for distribution by reducing spoilage, infestation, contamination, and pilferage. It also makes economical usage of warehouse space: conserves labour in both distribution and marketing, and permits distribution of identified products that can be effectively marketed through retail outlets such as supermarkets.

The choice of packaging for a given food product is controlled by a variety of factors, i.e. the food characteristics determine the protection needed to prevent deterioration, and the distribution system affects the products shelf-life and therefore imposes additional requirements for its protection. The food package must be attractive, convenient, and identifiable to the consumer. Its costs must be low, and in the environmentally friendly 90's the ultimate disposal of the used package must also be considered.

From the very start of civilisation mankind has had many competitors for the food he produces. Particularly animals, such as rodents, insects and micro-organisms, each of which cause wastage at various stages in the growth, harvesting, processing, storage, transport and sale of food. If micro-organisms are permitted to flourish in foods, this can lead to pretty devastating results. Normally micro-organism growth manifests itself in the form of a mould or putrefaction of the food, however, other organisms such as bacteria can render the food poisonous to man, thereby causing sickness and even death. Microbial spoilage can usually be attributed to physical properties such as gain or loss of water. In food products with high water contents, such as fresh produce or meat, water loss alters physical characteristics, and water gain can lead to favourable conditions for microbiological growth. Under these circumstances the function of food packaging is to ensure against gain or loss of water. Almost all of the above adverse reactions are accelerated by increasing temperature.

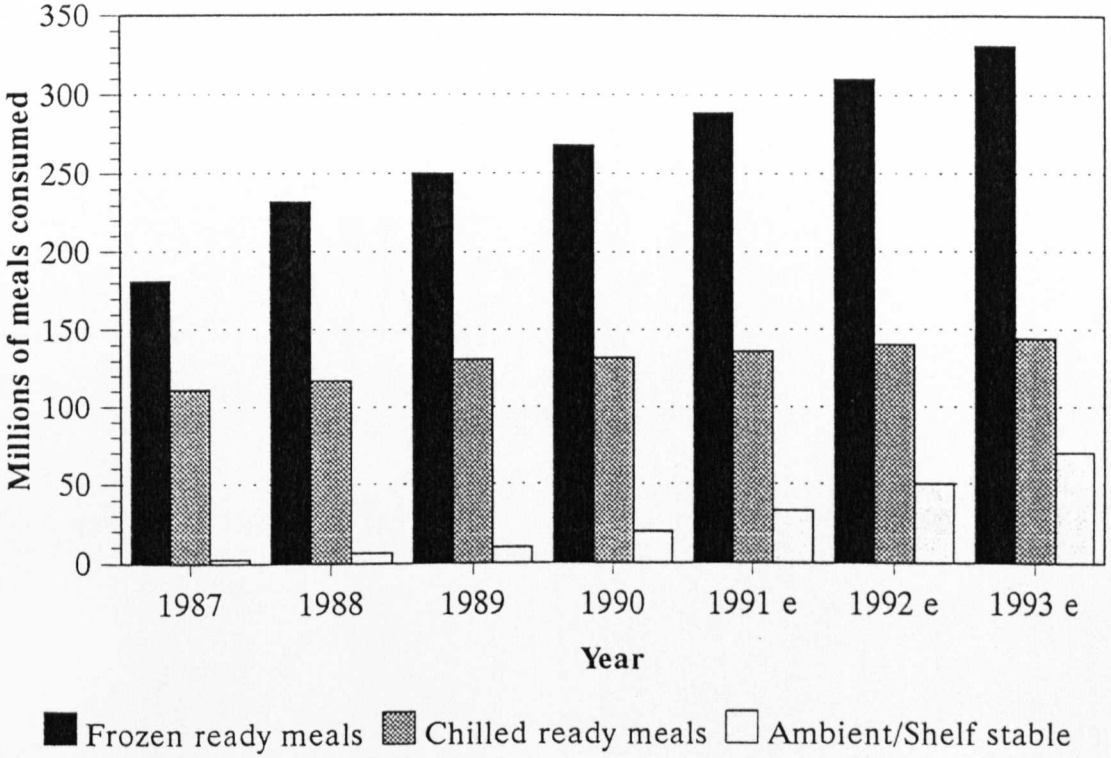
1.2 PLASTIC PACKAGING

A range of materials are used in food packaging applications including, glass, paper, cardboard, tinned steel and aluminium cans and foil. However, the use of plastic as a packaging material is rapidly increasing (1). Plastics offer both the manufacturer and the customer several advantages over other packaging materials. Not only does plastic packaging provide a means of presenting foods in ways not previously possible, it also plays a role in the marketing of trendy packaging, with easy fabrication and printing properties. Light weight and good durability, when compared with glass and paper, give plastics extra advantages to both the bulk shipment of food and the movement of the supermarket trolley. Plastic films with ready sealability and a good control of permeability provide a convenient mechanism for presenting food to the consumer in single meal portions. Demographic and social changes have also contributed to the increasing use of plastic. More individuals are now preparing their own meals and this has increased the demand for easily prepared meals (Figure 1.1). It is this convenience approach which is increasingly in tune with the modern world where a meal can be prepared in a few minutes either by boiling a bag or heating a tray in a microwave. The presence of microwave ovens in most homes can be highlighted as being a key factor in the increasing use of convenience meals. Convenience meals or ready meals as they are sometimes called can be split into three distinct groups, frozen, ambient or chilled.

Ambient or shelf stable meals are designed to have a shelf life of up to twelve months, but this is very much dependant on the type of food packaged. Examples include pot noodles, chillies and curries. Chilled meals are defined as being chilled to a maximum of 10°C and a minimum of 0°C, the aim being not to allow ice crystals to form in the product, but at the same time prolonging the shelf life of the food. Examples of such meals include kippers and sausage meats. Frozen meals have the largest sales of the three groups primarily due to the large variety of foods that are packaged in this manner. The food is usually heated whilst still within the packaging either by using a microwave or conventional oven. Complete meals laid out into portions in a tray are available in this format as are trays containing spicy Oriental foods, and boil in the bag fish.

1.3 PLASTIC MATERIALS USED FOR PACKAGING

A range of polymers are used for food packaging applications, and the principle materials used are detailed below. Other polymers are used but they tend to be used for specialised applications and are of low scale use.



Note :- e = estimate

Figure 1.1 UK sales pattern for ready meals (1)

1.3.1 Polyethylene

Polyethylene is very inexpensive, chemically stable, relatively easy to seal, tough with a large strain potential, and can be employed over a wide temperature range. Additionally, it is an excellent barrier to water vapour, but only average with regard to the permeability of gases, aromas, and fats. Barrier properties increase with increasing density, as does the degree of crystallinity, strength, stiffness, hardness and melting point. Contrary to this, the toughness, impact strength, transparency, sensitivity to reduced temperatures, and resistance to stress cracking decreases with increasing density.

Low density polyethylene (LDPE) is the least expensive material and is mainly employed for films, coatings and laminating purposes. Linear low density polyethylene (LLDPE) is increasingly being employed as a replacement for LDPE because of its increased strength and toughness. LLDPE is used most frequently for sealing layers in laminates, freezer bags, stretch films, shopping bags and sacks for heavy goods. High density polyethylene (HDPE) as a result of its increased stiffness and impermeability to fats is

commonly used in the packaging of meat, and extrusion blow moulded into bottles for milk and water.

1.3.2 Polypropylene

Polypropylene (PP) like polyethylene is one of the least expensive mass produced polymers. As with polyethylene, the water vapour barrier properties of PP are good, lying between those of LLDPE and HDPE. However, it is only has average impermeability to gases and aromas, but is generally a better barrier than LLDPE to fats.

Standard PP film is rarely used for packaging purposes because below 0°C it becomes brittle. To improve flexibility it is usually copolymerized with ethylene. As a copolymer it is used in the production of injection moulded containers for frozen foods such as ice cream, heat sealing layers for retort packaging, steam sterilizable cups and menu trays that can be warmed in a microwave oven, and houseware utensils such as kettles. Biaxially oriented PP improves its mechanical strength, impermeability, transparency and stability to reduced temperatures (-50°C). In this form it is used to wrap bakery products, and as laminated plies for crisps, and numerous other flexible pouch wrapping applications. It is also now increasingly being used in the packaging of confectionery products

1.3.3 Polyvinyl chloride

To be converted into a film polyvinyl chloride (PVC) must be modified with heat stabilizers and plasticizers, which increases its cost. Plasticized PVC is highly transparent and soft, with a very high gas permeation rate, but low water vapour transmission. As a film PVC is principally used to package red meat and poultry produce. Sparkle and transparency, combined with the ability to transmit oxygen to maintain red meat colour, are the main advantages of this film. However, health hazards associated with the use of PVC stretch films containing plasticizers and residual monomers has generally led to replacement by other polymers. Biaxial orientation improves the impermeability and strength of PVC, but again bottles for mineral water and cooking oils, made from this material are being replaced by polyester versions.

1.3.4 Thermoplastic polyesters

The term thermoplastic polyesters refers to a group of high quality polymers of which polyethylene terephthalate (PET) is the most significant. Films made from PET have intermediate gas and water vapour barrier properties, very high tensile and impact strengths and high temperature resistance. Applications include uses as an outer web in laminations to protect aluminium foil, or as baking trays for hot air ovens at temperatures ranging from 200 to 220°C. It is also increasingly being used in the bottling of sparkling beverages.

1.3.5 Polyamides

From the approximately 20 different polyamides / nylon (NY) products presently available, the most important in terms of packaging are NY 6, NY 12, NY 6/6 , NY 6/12 and NY 11 (numbers corresponding to the number of carbon atoms between NH groups). Polyamides are high quality polymers in the mid to high price range. Depending on the degree of crystallinity, they vary from highly to relatively transparent; they have high strength and toughness, average hardness and stiffness, and are relatively impermeable to gases, aromas, and fats. Because of their hydrophilic character, polyamides tend to be a poor barrier to water vapour.

Polyamides as monofilms (NY 6, NY12) are generally used for the packaging of frankfurter type sausages. However, the primary use of polyamides is in the manufacture of laminates, particularly in combination with polyolefins, which complement the properties of polyamides with favourable water barrier and sealing characteristics.

1.3.6 Polystyrene

The advantage of standard polystyrene lies in its excellent clarity, stiffness, and dimensional stability. However, because of its high permeability to water vapour and gases it is typically used as a packaging substrate for short term storage of refrigerated low fat content dairy products e.g. yoghurt, cottage cheese, and cream. Polystyrene is also used in trays for fruit, eggs, baked goods, and confectionery. In addition, foaming polystyrene resin prepared by blending with gas delivers an opaque, low density sheet which is used as plates and insulated hot beverage containers. Copolymers of styrene tend to have higher impact strengths and improved oil and aroma stability. The main copolymers used are acrylonitrile butadiene styrene (ABS), styrene acrylonitrile (SAN), and styrene butadiene (SB).

1.4 ADDITIVES IN PLASTIC

It was realised early in the development of the plastics industry that to obtain better products, additives needed to be added to the base polymer. These additives are designed to enhance the properties of the parent polymer without appreciably altering its chemical structure. Additives can be conveniently classified according to their function into various classes and subdivided according to their more specific purposes as shown in Table 1.1 below.

Main Classification	Subdivision
A) Processing Additives	i) Processing stabilizers ii) Lubricants iii) Viscosity depressants iv) Fusion promoters
B) Flexibilizers	i) Plasticizers
C) Anti-ageing additives	i) Antioxidants ii) Antimicrobials iii) Ultraviolet stabilizers
D) Surface property modifiers	i) Antistatic agents ii) Antifogging agents iii) Antiblocking additives
E) Optical property modifiers	i) Pigments and dyes ii) Nucleating agents
F) Fire retardants	i) Ignition inhibitors ii) Self-extinguishing additives iii) Smoke suppressants
G) Foaming additives	i) Blowing agents

Table 1.1 Additives in polymers

1.4.1 Processing additives

The degradation of polymers frequently involves oxidation reactions by a free radical mechanism, and at high temperatures, interaction of oxygen with the polymer leads to the formation of hydroperoxide groups. These decompose into very reactive HO• radicals, which lead to molecular scissions. Since it is practically impossible to eliminate oxygen from the

system, additives are used to inhibit oxidation reactions. These additives include primary and secondary stabilizers, and chelating agents. Primary stabilizers (antioxidants) such as hindered phenols or aromatic amines interrupt the oxidation chain reaction by combining with any free radicals. Secondary stabilizers (peroxide decomposers) such as organic thio-esters, phosphites and metal thiocarbamates react with the hydroperoxides as they are formed. Finally, chelating agents (metal deactivators) such as organic phosphites and hydrazides protect the polymer by immobilizing metal ions through co-ordination reactions.

In addition to the aforementioned processing additives some polymers such as polyolefins have a tendency to stick to metal parts of the machinery during processing. This is reduced by adding lubricants such as polyethylene waxes, fatty acid esters, amides and zinc stearates to the polymer.

1.4.2 Flexibilizers

In order to make brittle polymers such as PVC suitable for flexible films and containers plasticizers have to be added. These plasticizers also give the material the limp and tacky qualities found in cling film. The most common plasticizers used in PVC are typically phthalic esters such as dioctyl phthalate, and dioctyl adipate.

1.4.3 Anti-ageing additives

Ageing of a polymer is essentially the deterioration of the material from the combined effects of atmospheric radiation, temperature, oxygen, water, micro-organisms and other atmospheric agents. It is customary to use the term ageing to indicate that a chemical modification in the structure of the material has occurred. Antioxidants have already been mentioned under processing aids, but they are also necessary in polymeric films such as polyolefins which degrade in the atmosphere. Usually a combination of different antioxidants are used together for synergistic effects.

Antimicrobials such as algaecides, bactericides and fungicides are sometimes added to polymers to prevent the growth of micro-organisms. However, their use in food packaging is rare because of the possibility of migration into the food itself.

UV stabilizers are also used in polymers to prevent deterioration of polymeric films by photo-oxidation. They act by absorbing high energy UV radiation and releasing it as lower energy radiation.

1.4.4 Surface property modifiers

Antistatic agents are used to prevent the accumulation of electrical charges in polymeric films, an undesirable effect caused by the fact that polymers are non-conductors of electricity. The addition of ethoxylated fatty amines, polyhydric alcohols and derivatives, and non-ionic and quaternary ammonium compounds overcomes the problem; they migrate to the surface and form a conducting layer through the absorption of atmospheric moisture. Many polymer films also have a tendency to stick together due to them being non-conductors of electricity. This tendency to stick together can be reduced by the addition of organic amides such as erucamide, and metallic soaps such as zinc and calcium stearate.

In some food packaging applications, moisture tends to condense as droplets and obstructs the view of the pack contents. The addition of non-ionic ethoxylates or hydrophilic fatty acid esters such as glyceryl stearate promote the deposition of continuous films of moisture.

1.4.5 Optical property modifiers

The majority of polymers used for food packaging films are uncoloured, but sometimes polymers are coloured by the addition of colourants. The principal pigments for use as colourants in polymers are carbon black, white titanium dioxide, red iron oxide, yellow cadmium sulphide, molybdate orange, ultramarine blue, blue ferric ammonium ferrocyanide, chrome green, and blue green copper phthalocyanides (2).

1.4.6 Fire retardants

Although most food contact polymers are combustible, their lack of flame resistance is disregarded in most food packaging applications. This is quite a reasonable approach, considering that the risk of fire; from e.g. polystyrene cups, must be balanced against the possible toxicity of flame retardant additives.

1.4.7 Foaming agents

Foaming or blowing agents are used for the production of cellular products and are normally classified into physical and chemical types, according to whether the generation of gases to produce the cells takes place through a physical transition (i.e. evaporation or sublimation) or by a chemical process (i.e. decomposition reactions which result in the evolution of gases) (3). For example, expanded and extruded polystyrene foams use a physical blowing agent such as a fluorocarbon or pentane.

1.5 MIGRATION PHENOMENA IN POLYMERS

In food contact plastics, not all of the types of additives mentioned in Section 1.4 are used, and those which are must of course have received clearance by the appropriate food regulatory authorities. However, these additives, their resulting degradation products, plus any residual monomers from the polymers production have the potential to migrate from the polymer into the food.

In food packaging terminology, migration is generally used to describe the transfer of substances from the polymer to the food. Substances that are transferred to the food as a result of contact or interaction between the food and the polymer are often referred to as migrants. However, it is important to note that migration is a two way process since constituents of the food can also migrate into the polymer. For example the sorption of key aroma and flavour compounds in fruit juices by plastics has been reported (4). In addition, compounds present in the environment which surrounds the packaged food can be absorbed by the packaging and migrate into the food. For example diesel and petrol vapour have been detected in wrapped bakery and confectionery products (5), and off-odours have been reported due to residual printing inks solvents (6,7).

It is important to distinguish between overall migration (originally referred to as global migration) and specific migration. Overall migration is the sum of all (usually known) mobile polymer components released per unit area of packaging material under defined test conditions, whereas specific migration relates to an individual and identifiable compound only. Overall migration therefore is a measure of all compounds transferred into the food whether they are of toxicological interest or not.

The migration of molecules from polymers into food is a complex phenomena, and according to present day interpretations it is a diffusion problem (8). The extent of migration from a polymer depends on numerous variables, but particularly on the thickness of the polymer (9), the concentration of the components in the polymer (10), the time of contact between polymer and foodstuff (11), the temperature (11), and on the physico-chemical properties of the components of the system 'polymer / low molecular weight components / foodstuff.

In most cases, migration from a polymer sheet into a food can be described by using Fick's second law (12). A solution of this equation describing the amount of substance, M_t , migrating into the food in time t, divided by the area A of the membrane, is (13):

$$J \cdot t = \frac{M_t}{A} = 2 \cdot Cp_0 \cdot \left(\frac{\beta}{1+\beta}\right) \cdot \left(\frac{Dp \cdot t}{\pi}\right)^{1/2}$$

where :-

$$\beta = \left(\frac{1}{K}\right) \cdot \left(\frac{Df}{Dp}\right)^{1/2}$$

and Cp_0 is the initial concentration of a migrant in the polymer. The equation shows that the magnitude of the diffusion coefficient (Df and Dp) in both the food and the polymer phases, respectively are important. The partition coefficient K gives the ratio of the concentration in the polymer to that in the food. In most cases, Df is orders of magnitude greater than Dp, so that $\beta >> 1$ and the migration is controlled by the slower diffusion of the migrant in the polymer phase.

The equation also shows that M_t is proportional to the square root of time. This is a common result in the initial stages ($\leq 60\%$ of the migrant is lost) of migration from polymers into food (13, 14). Mathematical solutions of Fick's second law for cases involving different volumes, types of food phase, fixed or agitated systems, or boundary layers have also been discussed (12, 15). It should also be noted that food components may penetrate into the plastic and, by doing so, distinctly accelerate the migration of low molecular weight components into the food. In most cases there is a direct correlation between the penetration ability of food components into polymers and the migration of low molecular weight components into the food (16).

Obviously food safety is an important issue and because everyone must consume food to live, the safety of food is an especially emotive matter. Most concern usually focuses on food additives, both those added intentionally to the food and those ending up in the food from, for example, the packaging material or processing equipment. Because migration has important legal consequences, this has led to the development of European community legislation governing food contact materials and articles.

1.6 EUROPEAN COMMUNITY REGULATIONS ON FOOD CONTACT MATERIALS AND ARTICLES

Not many of the materials suitable for food contact applications are completely inert towards foods, and those that are inert often have to be used in conjunction with other materials that are not inert. Any substance that migrates from food contact plastics into a food is of concern if it could be harmful to the consumer or has a deleterious effect on the food. Such effects might include the migration of toxic species from the plastic into the food, or the transmission of substances from the plastic into the food which manifests itself in the form of a taint that the consumer can detect. The care taken to produce wholesome and attractive foods must be matched by the care taken to see that the material in contact with it is compatible. For many years now food manufacturers and packaging suppliers have worked together to achieve this.

In the past it was the responsibility of organisations such as the Food and Drugs Administration (FDA) in the USA, and the national governments of each country in Europe to ensure the safety of food contact plastics. In the UK the laws and regulations governing food contact materials have always been very simple. They require, essentially that the material should not transfer to the food any constituent that would render the food unfit to eat. According to the materials and articles in contact with food regulations of 1978 (17), it is an offence to offer food for sale unless it is safe, fit to eat and of the substance and quality demanded. It is not surprising therefore that with such a controversial subject, other countries had their own ideas and legislations, which varied from those in the UK. This has now changed in Europe, and from the 1st January 1993 there is harmonised legislation on all European Community (EC) member states in respect of plastic materials and articles intended for use in foodstuffs.

1.6.1 Review of EC regulations to date

In 1973 the EC initiated a programme for the harmonisation of legislation on materials and articles intended to come into contact with foodstuffs. The reasons for this action were to remove technical barriers to trade between member states and to protect the consumer from any risks associated with hazardous components in food contact materials. The starting point was to establish a framework directive under which specific directives relating to particular food contact materials could be adopted.

The key provision of the materials and articles framework directive 76/893/EEC, now replaced by directive 89/109/EEC (18) is that materials and articles shall be manufactured in

such a way that under normal conditions of use they do not transfer their constituent to foods with which they are in contact, in quantities which could endanger human health, or cause unacceptable organoleptic changes in food. In order to reinforce its general provisions, the framework directive provides for specific directives to be developed for individual food contact materials and lists the various measures that these directives may include. The framework directive also specifies that such specific directives shall be adopted by unanimous agreement among member states. Regrettably, as the community has grown, unanimity has become increasingly difficult to achieve. However, several directives have already been agreed and the majority of these have either been implemented in UK law or are being so implemented (see Table 1.2).

During the 1970's the community worked on a directive to limit the overall or global migration of the constituents of plastics into food. A directive in 1982 laid down the basic rules for the testing of plastics for all purposes 82/711/EEC (19). It was originally planned to cover all relevant aspects, positive list, specific migration and organolepsis. However, it soon became clear that this was a monumental task and the simpler method of an all embracing global or overall migration limit was introduced, which was already in operation in France and Italy. This was strongly opposed at first by the British, German and Irish governments and modified versions were proposed. Eventually this lead to the production of the new framework directive 89/109/EEC which contains requirements for:-

- A positive list of monomers and other starting materials.
- Overall migration limits using the 4 specified food simulants.
- Specific migration.

1.6.2 The plastics directive

As a result of framework directive 89/109/EEC the commission produced a specific directive relating to plastic materials intended for use in contact with foodstuffs 90/128/EEC (20). Directive 90/128/EEC is often called the 'plastics' directive and it deals with the overall migration limits for chemicals migrating from plastics, and lists the monomers and other starting materials which may be used in the manufacture of plastics intended for food contact applications. It must be stressed that currently this directive applies only to plastic materials and articles and parts thereof which consist exclusively of

Number	Subject	Adoption	Entry into Force
76/893/EEC	Framework directive on food contact materials and articles	23/9/76	26/11/79
78/142/EEC	Plastics: Limits on vinyl chloride monomer (VCM)	30/1/78	26/11/79
80/590/EEC	Symbols that may accompany materials and articles	9/6/80	1/1/81
80/766/EEC	Plastics: Determination of VCM in finished products	8/7/80	11/1/82
81/432/EEC	Plastics: Determination of VCM in foods	29/4/81	1/10/82
82/711/EEC	Plastics: Basic rules for testing migration	18/10/82	to be determined
83/299/EEC	Regenerated cellulose film	25/4/83	1/1/85
84/500/EEC	Lead and cadmium released from ceramics	15/10/84	16/10/87
85/572/EEC	Plastics: List of simulants for testing migration	19/2/84	to be determined
86/388/EEC	Regenerated cellulose films: Limits on MEG & DEG	23/7/86	1/4/87
89/109/EEC	New framework directive on food contact materials and articles, replacement for 76/893/EEC	21/12/88	10/7/90
90/128/EEC	Plastics: Monomers	23/2/90	1/1/91
92/39/EEC	Plastics: Monomers 1st amendment	14/5/92	1/1/93
93/8/EEC	Plastics: Basic rules for testing migration 1st amendment	15/3/93	1/4/94
93/9/EEC	Plastics: Monomers 2nd amendment	15/3/93	1/4/94

Table 1.2 EC directives adopted on food contact materials and articles.

plastics, or are composed of two or more layers of materials, each consisting exclusively of plastics, which are bonded together by means of an adhesive or by any other means. This directive which will be amended and updated at appropriate times as new information becomes available, contains two annexes which are really the heart of the document. Already the first and second amendments to this directive have been published (92/39/EEC (21) and 93/9/EEC (22)) and approved by the EC.

Annex 1 of 90/128/EEC deals with the provisions applicable when checking compliance with the overall migration limit. It states that plastic materials and articles shall not transfer their constituents to foodstuffs in quantities exceeding 10mg dm^{-2} of surface area of the material or article (overall migration limit). The overall migration limit of 10mg dm^{-2} is a 'catch all' politicians number which was agreed on by the commission from its very initiation. However, this limit is 60mg kg^{-1} of foodstuff for containers of between 0.5 and 10 litre capacity, and articles for which it is impracticable to determine the surface area in contact with the foodstuff. This figure of 60mg kg^{-1} foodstuff is obtained by assuming a 1kg block of food is packaged in the form of a cube with each of the six sides having a surface area of $1dm^2$ in contact with the food. The basic rules for testing migration levels of components into foods are laid down in EC directives 85/572/EEC (23) and 93/8/EEC (24). These set out the simulating liquids to be used for the various foodstuffs (Table 1.3 and 1.4) and the contact times and temperatures to be used in the migration tests (Table 1.5).

Simulant A: Distilled water or equivalent

Simulant B: 3% w/v acetic acid in aqueous solution

Simulant C: 15% v/v ethanol in aqueous solution

Simulant D: Rectified olive oil, synthetic triglyceride or sunflower oil

Note:- The selection of the simulant(s) to be used for any particular food is determined by reference to directive 85/572/EEC.

Table 1.3 Simulation liquids used in migration tests.

Foodstuff	Simulants to be used			
	A	B	C	D
Non alcoholic beverages, waters, tea, coffee, mineral water, fruit or vegetable juices of normal strength or concentrated	$X_{(a)}$	$X_{(a)}$		
Animal and vegetable fats and oils				X
Processed vegetables in the form of purees	$X_{(a)}$	$X_{(a)}$		
Fresh fish, chilled, salted or smoked	X			
Processed meats (poultry, ham, bacon)	X			X/4

where: X is the test liquid to be used.

$X_{(a)}$ one of the two simulants given should be used.

If pH > 4.5 simulant A should be used.

If pH < 4.5 simulant B should be used.

X/4 results of the test should be divided by four. Known as the 'reduction coefficient', which takes into account the fact that fatty food simulants have a greater extractive capacity than some fatty foodstuffs.

Table 1.4 Example taken from directive 85/572/EEC on the list of simulants to be used in migration tests.

It must be emphasised that the test should be carried out on the finished product in a manner representing actual conditions of use. This means that in addition to using the appropriate food simulant at the correct temperature for a specific period of time, it is necessary that only the parts of the sample intended to come into contact with foodstuffs shall be in contact with the food simulant. This necessitates the use of single sided testing for articles comprising several layers (i.e. boil in the bag laminates), although it is permissible to demonstrate the use of a more severe test. Where an article is intended to come into repeated contact with foodstuffs (i.e. plastic kettles), the migration test is carried out three times on a single sample using fresh simulant on each occasion. Compliance is checked on the basis of the third test, although if an article passes the first test no further testing is necessary.

Contact conditions during actual use	Test Conditions
Contact time	*Test time*
t ≤ 0.5 hour	0.5 hour
0.5 hour < t ≤ 1 hour	1 hour
1 hour < t ≤ 2 hours	2 hours
2 hours < t ≤ 24 hours	24 hours
t > 24 hours	10 days
Contact temperature	*Test temperature*
T ≤ 5°C	5 °C
5 °C < T ≤ 20 °C	20 °C
20 °C < T ≤ 40 °C	40 °C
40 °C < T ≤ 70 °C	70 °C
70 °C < T ≤ 100 °C	100 °C or reflux temperature
100 °C < T ≤ 121 °C	121 °C *
121 °C < T ≤ 130 °C	130 °C *
130 °C < T ≤ 150 °C	150 °C **
T > 150 °C	170 °C **

* Use simulant C at reflux temperature

** Use simulant D at 150 °C or 175 °C, in addition to simulant A, B and C used as appropriate at 100 °C or at reflux (See Table 1.3 for simulants).

Table 1.5 Migration tests for plastic material

Annex 1 of directive 90/128/EEC also specifies the methods of analysis that are to be used for determining the overall migration in addition to laying down the analytical tolerances of 20mg kg^{-1} (3mg dm^{-2}) for olive oil and 6mg kg^{-1} (1mg dm^{-2}) for aqueous simulants. If an aqueous food simulant is used, the total quantity of substances released by the sample is determined by evaporation of the simulant and weighing of the residue. For rectified olive oil or any of its substituents the sample of the material or article is weighed before and after contact with the simulant. The simulant absorbed by the sample is extracted and determined quantitatively. The quantity of simulant is subtracted from the mass of the sample measured after contact with the simulant and the difference between the initial and corrected final mass represents the overall migration of the sample examined.

A major limitation of overall migration tests is that no attempt is made to identify the migrating substances which may or may not be harmful to the consumer. Since no identification of the material migrating is made the overall migration can at best be regarded only as a poor measure of the inertness of the material and has little to justify it

on a scientific or toxicological basis. It is therefore necessary in cases where monomers are suspected of being potentially toxic to develop new methods of analysis that are capable of detecting low levels of specific monomers that have migrated from food contact plastics into food simulants.

1.6.3 Monomers

Annex 2 of directive 90/128/EEC lists the monomers and other starting materials which may be used for the manufacture of plastics intended for food contact. The monomers in this section have been evaluated by the Scientific Committee for Food (SCF), which is the expert advisory body set up by the EC in 1979 to advise them on toxicological matters. The SCF have looked at 600 or so monomers and graded each on a scale 0 - 9 (25) (see Table 1.6) according to the information available. As can be seen from Table 1.6 the SCF assesses the monomers in terms of Acceptable Daily Intake (ADI) and Tolerable Daily Intake (TDI). The ADI of a chemical for humans is defined as the daily intake that during an entire lifetime appears to be without appreciable risk on the basis of all known facts at the time. It is expressed in mg kg^{-1} of body weight. This is calculated by dividing the highest dose level that causes no significant adverse effects, by a safety factor, in most instances of 100 - 1000. The TDI is similar to ADI but is based on the maximum amount of a chemical that a human can take in one day without causing any deleterious effects. From all the toxicological data supplied by the SCF the commission interpreted the information to produce two sections, A and B, for Annex 2.

Section A is made up of those monomers classified by the SCF in lists 0,1,2,3 and 4, and considered to be safe starting materials. Since these monomers have been classified as safe starting materials they may be used in the manufacture of food contact plastics in all EC states, and no state can refuse the import of any plastic food contact material made from a monomer listed in section A of Annex 2. In addition to listing the monomers which can be used it lists any restrictions which may exist in respect to residual monomers (Qm) in the final plastic products, or a specific migration limit (SML) of a monomer into the specified food simulants.

There are about 40 substances in the current list of 200 monomers in section A for which a specific migration limit into the food or appropriate food simulant is given. When a monomer with a SML is used to produce a plastic material for food contact, a specific migration test for that monomer on the finished article must be carried out.

Moreover the sum of all the specific migrations must not exceed the overall migration limit of 10mg dm^{-2} or 60mg kg^{-1} of food. The only problem with the requirement for a SML is that in most cases there is no agreed test method. Originally when the overall migration concept was accepted several years ago, it was on the understanding that this would remove the necessity of a specific migration test in most areas. Clearly no one could object to a SML when the monomer is a human carcinogen, or is suspected of being one. Therefore, it is the objective of all polymer manufacturers to have all the monomers they use in the production of food contact plastics listed in section A, preferably without any restrictions. In most cases this is not possible and the majority of monomers are listed in section B.

Section B contains a list of those monomers which are either at present approved by at least one or more member states, or are new monomers. They may continue to be used by that member state which has issued approval and others which recognise the approval status adopted. However, due to a lack of toxicological data the SCF is unable to express an opinion on these monomers. Eventually the aim is to get all the monomers transferred from section B to section A. Any monomers that remain in section B will be deleted, but this is unlikely to occur with those of real interest to the polymer manufacturers, who are taking the necessary steps to get the monomers transferred.

In order to keep a monomer listed European industry is required to notify the EC that retention is required, and to provide the SCF with the necessary toxicological data required to get the monomer transferred from section B to A. The first step is to determine the residual monomer content in the plastic itself, and if this is detectable, determine the specific migration into food simulant. Normally the latter determination is done in olive oil at 40°C for 10 days. Some monomers will hydrolyse, and if the hydrolysis is virtually 100%, as is the case with some esters which are converted to the corresponding acid and alcohol, then no toxicological testing of the esters is required. In those cases where no or only partial hydrolysis occurs, the toxicological testing requirements depend upon the specific migration results. The lower the specific migration limit, the lower the number of toxicology tests with the minimum being three mutagenicity tests.

Annex I Substances for which the commission was able to express an opinion

List 0 - Substances which can be used in the production of plastic materials and articles, e.g. food ingredients and certain substances known from the intermediate metabolism in man.

List 1 - Substances for an ADI (Acceptable Daily Intake) has been established by JECFA (Joint FAO/WHO Expert Committee on Food Additives) or this committee.

List 2 - Substances for which a TDI (Tolerable Daily Intake) has been established by this committee.

List 3 - Substances for which an ADI or TDI could not be established but where the continued use could be accepted.

List 4 - This is subdivided into sections A and B.

Section A: Substances for which an ADI or TDI could not be established but which could be used if the substance migrating into foods or food simulants is not detectable by an agreed sensitive method.

Section B: Substances for which an ADI or TDI could not be established but which could be used if the levels of monomer residues in materials and articles intended to come into contact with foodstuffs are reduced as much as possible.

List 5 - Reserved for substances which should not be used.

Annex II Substances with insufficient Toxicological or Technological data for the Committee to express an opinion

List 6 - Substances suspected of being toxic for which data are lacking or insufficient.

Section A: Substances suspected to have carcinogenic properties. Substances should not be detectable in foods or in food simulants by an appropriate sensitive method for each substance.

Section B: Substances suspected to have toxic properties (other than carcinogenic). Restrictions may be indicated.

List 7 - Substances for which some toxicological data exists, but for which an ADI or TDI could not be established. The additional specified information should be furnished.

List 8 - Substances for which no or only scanty and inadequate data were available.

List 9 - Groups of substances which could not be evaluated due to lack of specificity. These groups should be replaced by individual substances usually in use.

List W - 'Waiting List' Substances not yet included in the community list.

Table 1.6 Consideration of monomers by EC scientific committee for food

1.6.4 Plastic additives

The EC commission has made good progress with the compilation of a list of the additives which can be incorporated into plastics intended for food contact applications (26-27). As with monomers all 2000 substances are being evaluated by the SCF and it is anticipated that the first specific directive on additives will be published shortly. Draft SCF opinions are available on the majority of these additives and once again it appears that a large percentage will be classified into the equivalent of section B in the monomers list, due to a lack of necessary toxicological information. Industry will therefore have to decide which additives are important to them and carry out the necessary tests requested by the SCF, e.g. migration, toxicology and hydrolysis to ensure the transfer to the list of approved additives.

It is worth pointing out that additives are defined by the EC as substances which are incorporated into plastics to achieve a technical effect in the finished product, and is intended to be present in the finished product. They are also used to provide a suitable medium in which polymerization can occur. Examples of some additives include, antioxidants, antistatic agents, fillers, impact modifiers, plasticizers, release agents, solvents, stabilisers and UV absorbers. Whereas, substances which directly influence the formation of polymers are not additives and are classified as aids to polymerization. Examples of such acids include catalysts, cross-linking agents, initiators and polymerization inhibitors.

1.6.5 Future EC and council of Europe programmes on food contact materials

Currently the plastics directive 90/128/EEC and the impending plastic additives directive exclude a number applications for plastic materials destined for use in contact with foodstuffs, e.g. coatings, epoxy resins and silicones. These exclusions are currently being dealt with but it is not clear whether the details regarding coatings, epoxy resins and silicones will be dealt with within the framework of directive 90/128/EEC or will be the subject of separate directives. However, it is clear that the same basic method of control will be applied to these materials.

Whilst the EC has been dealing with the directive on plastic materials 90/128/EEC, two other topics; colourants in plastics and aids to polymerization, are currently under investigation by the Council of Europe. The Council of Europe and its subsidiary bodies are entirely separate institutions from the EC. Its membership is wider

and includes countries such as Sweden, Austria and Switzerland as well as the member states of the EC. It is primarily an organisation which discusses and makes recommendations on matters of common interest in the field of public hygiene. Member countries may include these recommendations in their own legislation although it is not mandatory unlike EC resolutions which are mandatory on member states within a stated time period.

A subsidiary body of the Council of Europe, the Committee of Experts on Materials coming into Contact with Food has been working on food contact materials for a number of years. It has carried out much original work in this field and initially concentrated on substances used in food contact plastics. This was in advance of the current EC activity. The committee has recognised that to continue with its work on classification of substances in plastics would be duplicating the work currently being undertaken by the EC. A number of potential problem areas not being tackled elsewhere have been identified and the committee has turned its attention to these. A resolution on the use of colouring matter and pigments in food contact plastics has been produced. This abandons the traditional methods of control adopted by the EC of producing a positive list of constituents, primarily because it would be difficult to produce and enforce. Instead, provided the specifications of purity of the pigment, dye or colourant are met and the transfer of colourants is non detectable it may be used.

The committee has also produced a resolution on aids to polymerization. The control scheme outlined in the document places limits on the residual aids to polymerization (i.e. catalysts), either in the finished plastic material which will contact the food or by migration into the food simulants. Unlike monomers it is virtually impossible to produce a list of all the aids to polymerization used. There are a number of reasons for this but the most important is that aids to polymerization are often complex substances and are present in the final product in very small quantities. Additionally a great deal of research and money has gone into the development of these materials and firms which have produced new catalyst systems would not want to divulge the exact chemical formulations to anybody. Most of these aids to polymerization are also not in the same chemical form in the finished product as when they were incorporated into the plastic, which makes it difficult to control these substances by a positive list system.

Moving away from plastics the Committee is also dealing with matters related to paper and board which come into contact with foodstuffs.

All of these programmes are actively supported by the EC and it is likely that adopted resolutions will form the basis of draft proposals for directives. Therefore, the future activities of the EC are largely dependant upon the progress made by the Council of Europe.

1.6.6 Implications of EC legislation on industry

There is no doubt that the increasing public concern over the safety and purity of food, even though it may to some extent be promoted by tabloid headlines, is accelerating the introduction of new legislation needed to implement EC directives. It is perhaps ironic that many of the initial problems in the food field were with virtually unpacked foods such as eggs and meat pies, and not with those foods preserved in their packaging. Nevertheless the implementation of directive 90/128/EEC has triggered changes in the food contact field.

Certificates of warrant from packaging suppliers are no longer sufficient for a packer to demonstrate that he has taken due diligence. As can be seen in Figure 1.2 the supply chain is complex, and the responsibilities which fall onto each sector in the food chain have been allocated along the following lines. The monomers, additives and other ingredients used in polymer manufacture will have to be on the appropriate positive list, and polymer manufacturers will be responsible for using only approved materials. If they want to use any new material not on the approved list they will have to get the necessary toxicological and migration testing done and obtain approval from the SCF prior to use.

The packaging converter will need an assurance from his polymer supplier that the material is approved and complies with the regulations. In some cases the polymer manufacturer will need to provide information on the residual monomer levels in the polymer as despatched to the converter. However, the converter will still have to get the finished product tested for both overall migration and specific migration in the most appropriate ones of the four EC specified food simulants, even though the polymer manufacturer should be able to supply such data. This is because the data will not have been obtained on the finished product and the new regulations insist on this.

The food packer receiving the film or container, who in some cases may be the retailer, will be in possession of all the facts, from the supplier. These facts state that the correct approved ingredients were used and the finished packaging has been tested and passed the tests for overall migration and specific migration etc. However, this may still

not be sufficient. It is the food that is contained within the packaging that is being sold for consumption, and to prove in a court of law that due diligence has been applied, the packer may be required to produce evidence that the food simulants used are appropriate to his food product and that his processing factors (hot or cold fill) did not increase the overall or specific migration.

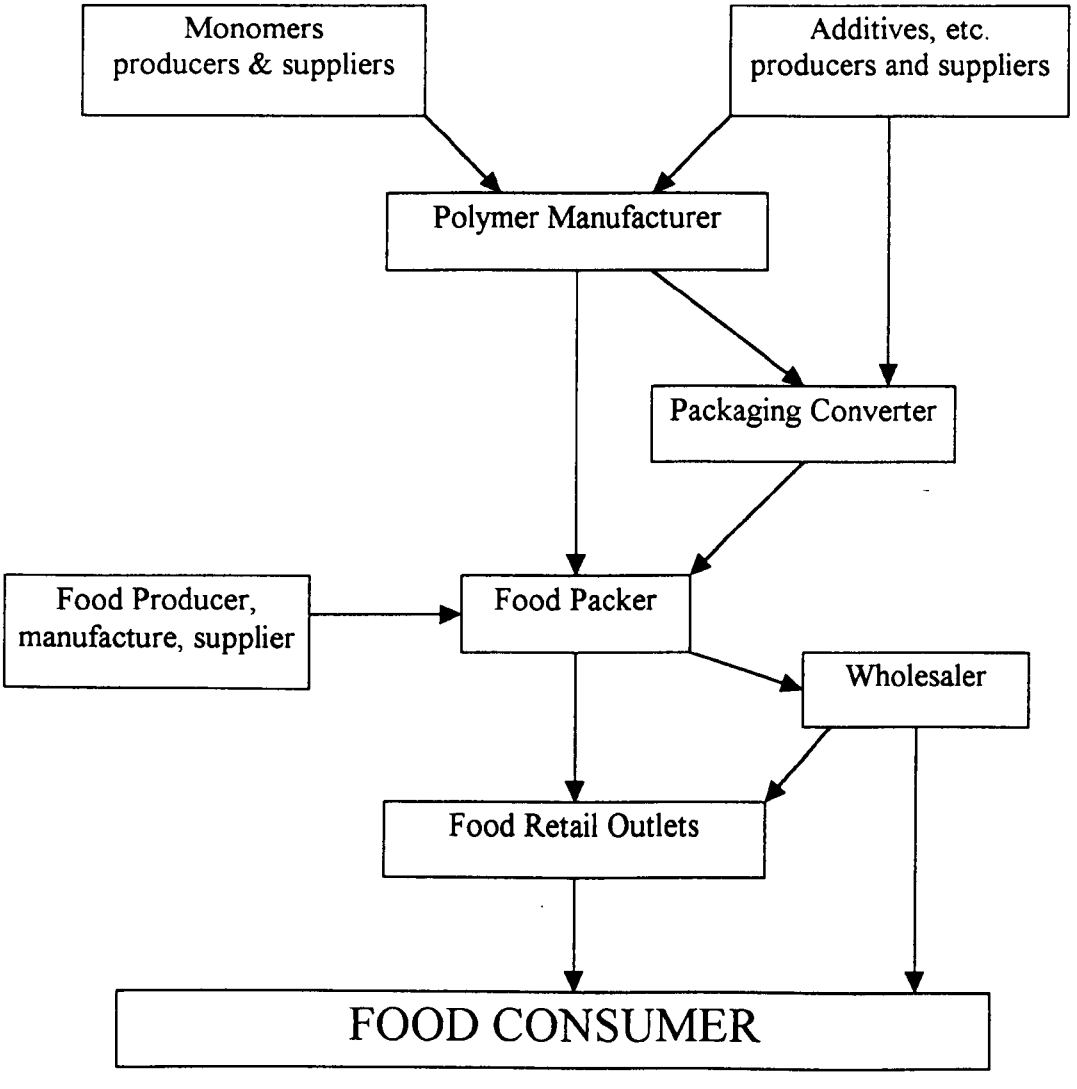


Figure 1.2 The supply chain (produced from information in reference 28)

The final link in the supply chain is the retailer and he may have to prove diligence by confirming the assurances of his suppliers by carrying out spot checks. After all the person who will be in court if the food is found to be contaminated is the retailer, and to defend himself he would probably have to prove that he took actions to check the assurances from his suppliers.

From the above considerations of the responsibilities of all participants in the supply chain from the raw material supplier to the retailer it can be seen that all have a role to play in ensuring that the consumer is presented with a food that is safe for human consumption. Thus everyone in the chain is likely to be involved and will be required to have some system for checking their products either in-house or by an outside laboratory. Suitable methods of analysis will also have to be developed to ensure that the product complies with the specific migration limits imposed.

It should be noted that directive 90/128/EEC is applied to all plastic materials and articles used in contact with food and not just packaging of foodstuffs. This means that articles such as cooking utensils, kettles, flasks and work surfaces used in the preparation of food are also included.

1.7 CURRENT PROJECTS

The Ministry of Agriculture, Fisheries and Food (MAFF) Food Science Laboratory in Norwich has been active in the migration area since 1975, providing surveillance data, developing new analytical methodology, and conducting research work on potential problem areas. The studies carried out have been conducted in close collaboration with the plastics industry and initial work concentrated on establishing the chemical identity of a full range of ingredients in commercial food contact polyvinylchloride (PVC) formulations, and in the foods they were in contact with (29-36). Other food contact materials which have subsequently been investigated include, polyvinylidenechloride (37), regenerated cellulose (38-40), polyethylene / polyisobutylene films (41), styrene (42-44) and its copolymer acrylonitrile-butadiene-styrene (ABS) (45-46). However, recent work has ranged from indepth studies of the migration of plasticizer from PVC 'cling films' into various foods and food simulants, to the investigations on the migration of oligomers and decomposition products from various food contact polymers used for conventional oven and microwave cooking.

In the work on plasticizers, migration of the standard PVC plasticizer di-(2-ethylhexyl) adipate (DEHA) from PVC 'cling film' into various foods and food simulants has been studied. The films included those for both retail packaging (47) and also domestic use, such as wrapping or covering food during storage and microwave cooking (48). Using the data obtained from these investigations on DEHA migrating from PVC films into foods a predictive mathematical model was evaluated and found to be in good agreement with data obtained on migration into fatty foods (49).

Migration of epoxidised Soya bean oil used as a secondary plasticizer and heat stabiliser in PVC has also been examined (50-52) as has acetyltributyl citrate (ATBC) used as a plasticizer for polyvinylidene chloride / PVC copolymer films (53-54). The analytical techniques employed isolation from the food / simulant by solvent extraction, size exclusion clean up and analysis by stable isotope dilution and gas chromatography with mass spectrometry multiple ion detection (55-58). More recently with the advent of polymeric plasticizers which can be used as complete or partial replacements for DEHA in PVC a series of investigations have been carried out on the migration of di-(2-ethylhexyl) phthalate and oligomers of polybutylene adipate from PVC into foods and food simulants (59-60). Their migration characteristics compared with DEHA in similar food applications have also been studied (61).

An extension of the plasticizer migration work investigated printed packaging films. Plasticizers are used in printing inks and although the printing is on the outer surface of the film it was shown that transfer of small amounts of the plasticizer from the printed surface to the food contact surface occurs on the reel (62).

The migration of substances which have propensity to migrate from materials is enhanced at elevated temperatures. In addition the elevated temperatures can generate new substances due to thermal decomposition. Consequently, attention has been given to studying the migration of substances from materials and articles which are used in microwave and conventional oven cooking. The MAFF laboratory has reported work on various materials and articles used in cooking, measuring the migration of plasticizers and antioxidants from films, oligomers from polyethylene terephthalate (PET) plastic containers and benzene from thermoset polyester cookware (63-67). The benzene in the thermoset cookware was found to originate from the polymerization initiator t-butyl perbenzoate. As a result manufacturers of these plastics have replaced the initiator with one that does not release benzene.

In addition MAFF has an ongoing series of research projects on migration and allied work which is contracted to various universities and other laboratories. These projects are under the direction of the working party on Chemical Contaminants for Food Contact Materials. The current topics include; studies to determine the levels of benzene and other aromatic hydrocarbons in plastic food packaging; studies to determine contaminants in food contact materials by neutron activation analysis; the development of migration test protocol for lacquer coatings on metal cans, and the identification of plastic oligomers with a potential for migration into food. Further allied projects are investigating the transfer of components from paper and board materials into and investigating aids to polymerization and monomer stability in polymers and food simulants (68).

In addition to MAFF other major laboratories around the world are engaged in migration research projects. The department of chemical engineering at the Massachusetts Institute of Technology in the USA has covered a wide range of work from theoretical studies to quantitative measurements of phenolic antioxidants migrating from ethylene-vinyl acetate (EVA) and polyolefins into foods and food simulants (69). In general they found that radiolabelled antioxidant migrations were largest for polypropylene (PP) from aqueous simulants, but for non-aqueous simulants the highest losses were from EVA followed closely by LLDPE. In both instances lowest losses were from HDPE.

The NATEC Institut in Hamburg, Germany has also carried out work on the migration of C^{14} labelled polymer additives into distilled water and the synthetic triglyceride fatty food simulant HB307. A range of common polymers were used with a variety of additives with different physical and chemical characteristics. The results showed that there was a direct linear relationship between the quantity of the additive which migrated and the initial quantity in the plastic. Other work carried out in the laboratory has compared 95% ethanol based food simulants with the standard fat simulant HB307 and olive oil, and found that the levels of migration of various additives from polyolefin samples were similar. Also in Germany the Fraunhofer-Institut in Munich has published a paper reporting the analysis of catty off odour produced from cook-in-the-bag ham products, packed and cooked in a polyamide-ethylene ionomer laminate pouch (6). Investigations showed that the odour was due to a hydrogen sulphide mesityl oxide adduct product, 4-methyl-4-mercaptopentan-2-one. The mesityl

oxide originating from the diacetone alcohol present in the printing, and the hydrogen sulphide from the packaged meat product.

The possibilities of using iso-octane as a fatty food simulant have been investigated by the TNO-CIVO Food Analysis Institute in the Netherlands (70). A wide range of plastics were used with this food simulant, and comparisons made with the results obtained by standard olive oil overall migration methods showed that they were generally in good agreement.

CHAPTER 2 : PROJECT OBJECTIVES

2.1 PLASTICS FOR NON-OVENABLE FOOD CONTACT APPLICATIONS

As can be seen in Chapter 1 the analysis of migrants from food packaging materials is quite a diverse and complex area. Therefore, in 1990 a research project was instigated by MAFF to investigate the transfer of migrants from non-ovenable food contact materials at elevated temperatures. The results of this work form the basis of this thesis. Migration can occur most readily when the polymer and its food contents are heated together. Heating can occur in a conventional oven, a microwave oven or by immersion in boiling water. The aim of the project was to identify and quantify species migrating from plastic materials into food when both are heated together in contact with boiling water.

There are two different situations to consider :-

- The boiling water is a heating medium only and is not part of the food chain.
- The boiling water is part of the food chain.

Initially a basket survey, of articles designed to come into contact simultaneously with food and boiling water was carried out in Leicester over the period August - September 1990. A variety of retail outlets were surveyed and Table 2.1 summarises these results in terms of the range of items in contact with food / water and includes an estimate of the contact time.

The basket survey indicated that plastic 'vacuum flasks', plastic kettles and boil in the bag meals have the longest exposure time to boiling water. When this is combined with the annual retail sales 7, 5, and 250 million items respectively (71,72,1), these items became the principal potential areas of investigation. Repeat use items such as kettles and flasks are referred to as utensils whereas the boil in the bag products are classed as packaging. As a general rule of thumb the plastic material used in utensils has a wall thickness of several millimetres whereas packaging film is around 50 - 150μm thick.

Item	Contact Time / min	Comment
Electrical		
Kettle - all plastic	180 +	Reheat
Kettle - part plastic e.g. lid	180 +	Reheat
Food Processors	30	
Coffee Makers	5 - 30	Type dependant
Teasmade	30 +	Reheat
Travel Jugs	30 +	Reheat
Housewares		
Cups / Thermos Cups	10 +	Cooling
Childs Unbreakable Flask	240 +	Lunch use (School)
'Thermos Flask' Plastic Insert	240 +	Soups etc.
Jelly Moulds	20 +	Cooling
Convenience Meals		
Pot Noodle	20 +	Single use
Slimmers (Boots)	15 +	Single use
Boil in the Bag	30 - 120	Single use

Table 2.1 Plastic food containers in contact with boiling water

2.1.1 Utensils

Several polymeric materials have been used in the production of plastic kettles since their introduction in 1983 (73). Acetal (polyformaldehyde) was used initially, but most modern kettles are injection moulded using filled and pigmented polypropylene.

The material used in childrens unbreakable flasks and flask inserts used to protect the conventional glass envelope were moulded from acrylonitrile butadiene styrene (ABS) material and filled polypropylene respectively (71). Within the remit of this project only the latter material was extensively studied. Schematic diagrams of typical kettles and flasks are shown in Figures 2.1 and 2.2.

2.1.2 Packaging films

It is important to be aware of the nature of the material used in the manufacture of the packaging of ready to heat meals. The nature of the packaging is to some extent defined by the method of storage prior to use, the material must have a range of physical properties

sufficiently wide to allow mechanical filling, deep freezing and the subsequent thermal shock of boiling water. The packaging must also be non-permeable to prevent taint from highly spiced foods affecting other foods stored in close proximity. There appears to be no single polymeric material that will meet all of these criteria and thus combinations of different polymer films have been developed for various applications. These films are either adhesively bonded together to produce laminates, or increasingly, are produced by coextrusion methods. In order to form a good bond between dissimilar materials such as nylon and polyethylene a tie layer is used in the coextrusion process.

In Europe boil in the bag food packaging is usually laminated from polyethylene and nylon 6 (74), with some films prepared from polyethylene and nylon 6,6 or polyethylene and polyethylene terephthalate (PET). The typical construction of a boil in the bag product is shown in Figure 2.3 and indicates that the polyolefin layer is in contact with the food and provides the advantage of a heat sealable material for rapid closure after filling. The outer layer of polyamide provides both the physical strength and non-permeability requirements of the pack. Typical total film thickness of a boil in the bag pouch is of the order 50 - 150μm. Food packaging is not manufactured in a single process, indeed there may be several steps involved and frequently a range of different specialist operators will work on the same item. The petrochemical industry initiates the process with the preparation of the polymer resins and additives which are transformed into films, and other materials, by the polymer manufacturer. Films are then sold on to converters who may print, laminate and prepare pouches from the virgin film. These packs are again sold on to the food packer and onto the retailer and finally to the customer (28).

Obviously, the potential migrants from a polymeric material range from residual monomers and polymerization aids through to degradation products, additives and other materials introduced during either extrusion, casting or injection moulding at the production stage.

2.2 MIGRATION EXPERIMENT PARAMETERS

The main driving force behind this research work is the adoption on the 1st January 1993 of legislation in all EC member states regarding the migration of monomers from food contact plastics. This legislation is covered by three main directives, each adopted by the EC. Directive 85/572/EEC (23) defines the food simulant which should be used for each foodstuff when carrying out migration testing and 93/8/EEC (24) specifies the test

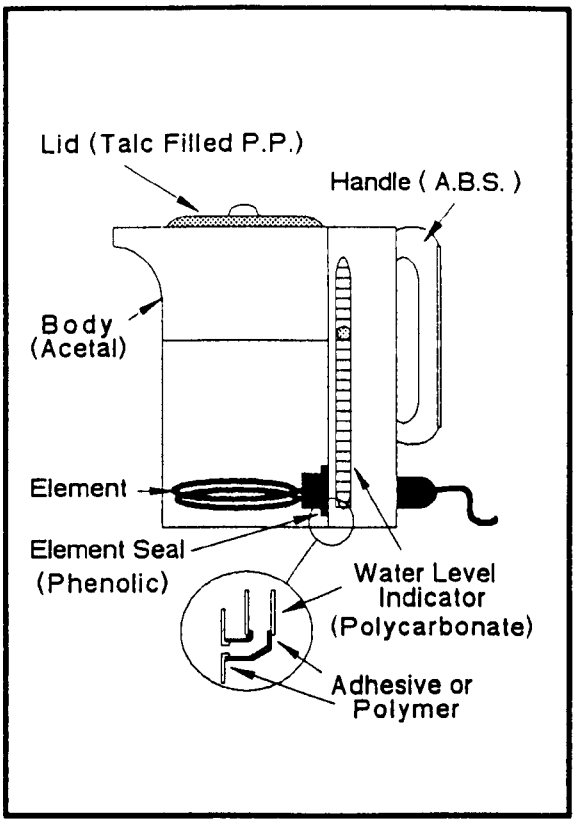


Figure 2.1 Schematic diagram of a plastic kettle.

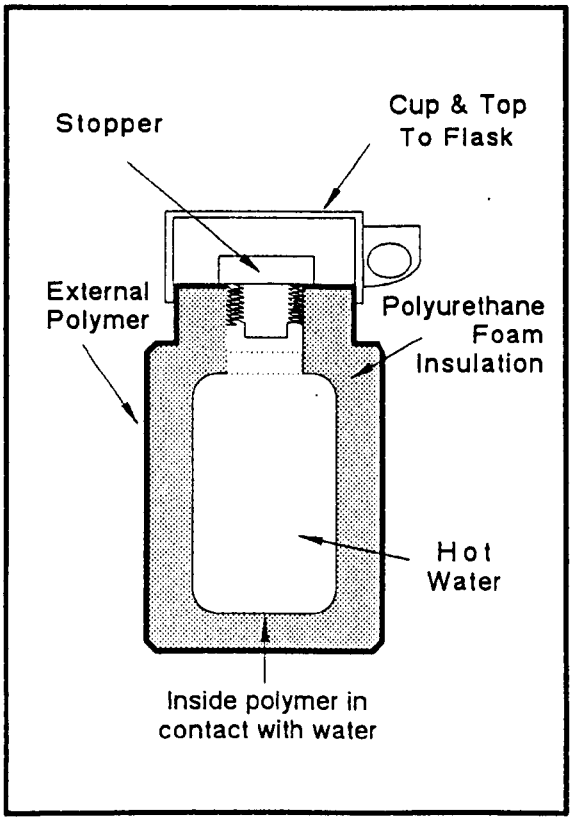


Figure 2.2 Schematic diagram of childs unbreakable flask.

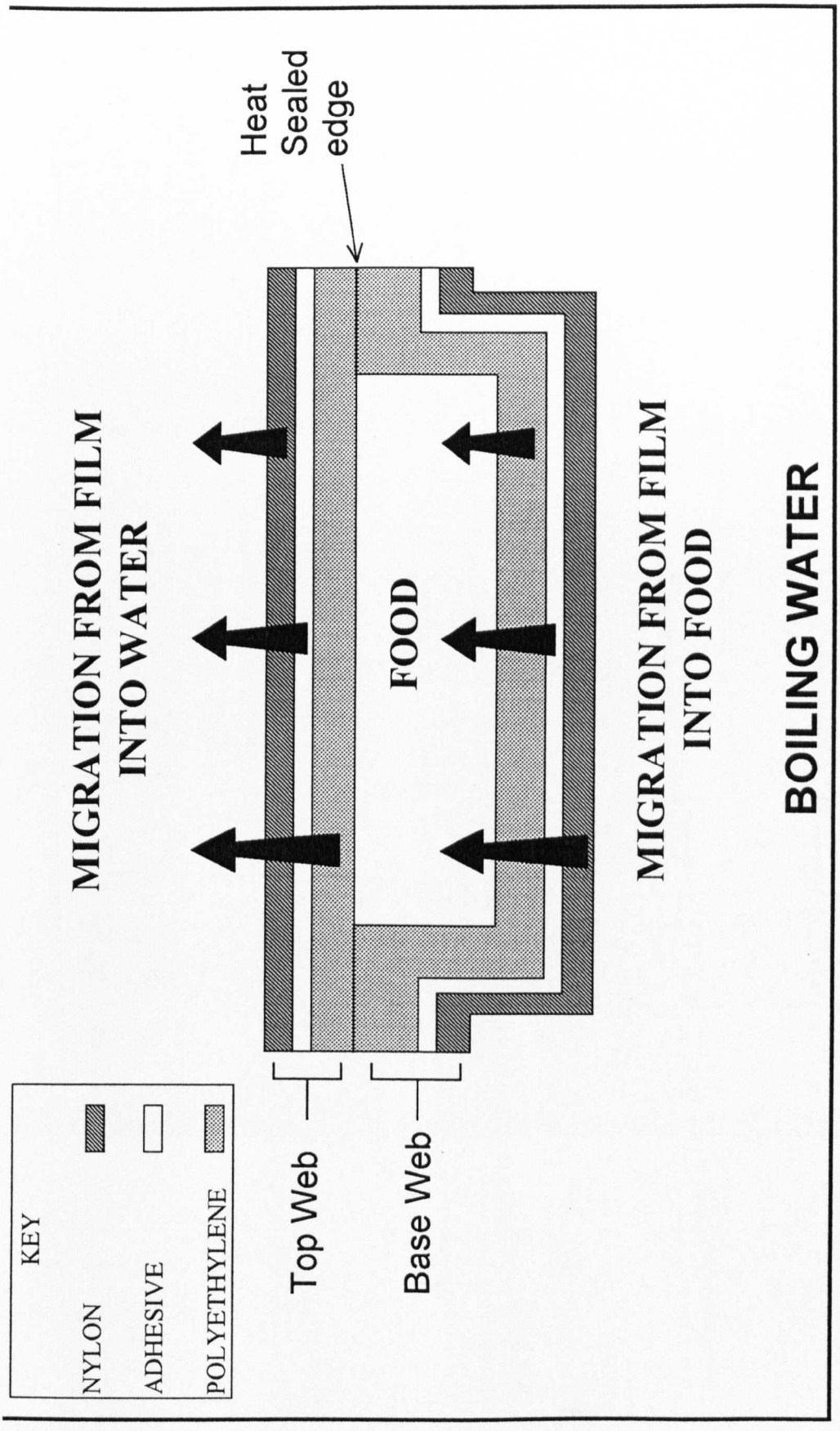


Figure 2.3 **Schematic diagram of boil in the bag packaging, indicating possible migration routes.**

conditions to be used. The plastics directive 90/128/EEC (20) sets out overall migration limits of 10mg dm^{-2} for chemical migration from plastic, in addition to stating what monomers may be used in food contact applications and specifying migration limits for the monomers. It is therefore necessary for polymer manufacturers, converters, packers and retailers to ensure that their products conform to these requirements. The impending plastic additives directive is expected to follow similar lines to the plastics directive. Therefore, it is one of the objectives of this project to develop methods of identifying the materials migrating from non-ovenable food contact materials into food simulants, and to ensure that they conform to the implemented restrictions.

The approach adopted was to examine both the final materials and also the individual components i.e. nylon, adhesive, polyethylene and polypropylene separately. Initially it was felt that only two food simulants, distilled water and olive oil should be utilized particularly if extended periods at 100°C were anticipated. The analytical investigations ranged from the determination of overall migration data, through gas chromatography-mass spectrometry (GC-MS) analyses to identify low molecular weight migrants; to high performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC-MS) techniques, to identify and quantify any material found in the food simulant.

2.2.1 Test conditions

A range of test conditions and polymer formats were used , but the fundamental test was exposure at boiling water temperatures for one hour or multiples thereof. Both the kettle and the flask can be readily tested in the single sided format which is quite appropriate to the in use conditions. Total immersion can also be used if allowance is made for edge effects and both faces are taken into account. For the boil in the bag material a pouch containing the simulant is the only really appropriate test format since the pouch is surrounded by water which acts as a plasticizer for the nylon outer layer. The use of a total immersion migration (75) test is therefore only applicable when water is the food simulant, and single sided testing using the PIRA cell (76) does not really match reality. It was therefore decided that the pouch, as used to contain the food, was the ideal test environment. In addition, the other test formats were used throughout this work to provide data for comparison. In particular a modification of the total immersion test, in which the polymer was chopped into 1cm squares prior to refluxing, was used

extensively during the development of the analytical methodologies. Pouches were prepared from either 21 × 11 or 11 × 11cm samples and were fabricated using a Hulme Martin dual electronic sealer where commercial examples were not available.

The migration test regimes can be summarised as detailed below:

Utensils

Chopped material	- total immersion in simulant	- 1 hour exposure
Chopped material	- total immersion in simulant	- multiple exposures
Commercial product	- single sided exposure to simulant	- 1 hour exposure
Commercial product	- single sided exposure to simulant	- multiple exposures

Films

Chopped material	- total immersion in simulant	- 1 hour exposure
Pouch format	- single sided exposure to simulant	- 1 hour in boiling water
Pouch format	- single sided exposure to simulant	- 1 hour in hot air oven

2.2.2 Materials tested

In this project the analytical techniques cited in Section 2.2 were used in combination with conventional overall migration determinations and an improved version of the Marcali method (77) for diamine measurements have been used to investigate a wide range of different plastic materials. Where possible each individual component of a boil in the bag pouch have been examined separately and in a range of combinations. The boil in the bag materials are representative of current western European practice and have included :-

- 24 specially prepared films where full manufacturing data is available
- 14 commercial materials supplied as pouches
- 10 different adhesive formulations

Significantly more results have been obtained from the study of aqueous food simulants as a result of the easier handling of the subsequent analyses after the migration period. In an attempt to alleviate the problems associated with the use of olive oil a low viscosity silicone oil (Dow Corning 200/50 cs from Merck /BDH) has been studied and comparison results for these two oils and with the aqueous medium have been obtained.

CHAPTER 3 : POLYOLEFINS

3.1 INTRODUCTION

Two polyolefins are principally used in food contact applications, polyethylene and polypropylene. Polyethylene is commonly used in film form for packaging applications, and polypropylene is often used in houseware items such as kettles, food processors and cooking utensils. However oriented polypropylene is now being produced as films with superior performance to polyethylene but at an increased cost.

Commercial large scale manufacture of polyolefins did not really start until the 1960's, which in comparison with other polymers was quite late. Despite this late start world-wide production of polyolefins has increased rapidly. World-wide polyethylene production in 1990 reaching $3.4x10^7$ tonnes capacity (78) and polypropylene output in 1992 $1.7x10^7$ tonnes (79).

3.1.1 Polyethylene

Low density polyethylene (LDPE) is produced by the free radical polymerization of ethylene under very high pressures (2,000 atmospheres) and elevated temperatures (200°C). Traces of oxygen initiate the free radical polymerization, but peroxides and hydroperoxides have been used as initiators.

In Europe consumption of LDPE in 1990 reached $4.6x10^6$ tonnes (80). One of the reasons for its widespread use is its versatility. It can be extruded into fibres, blown into bottles, injection moulded into closures and extruded as coatings on paper, aluminium foil or cellulose. As a film it is chemically resistant; especially to polar compounds, with good clarity and provides a good barrier to moisture and excellent heat sealability. However as a result of the polymer produced having a highly branched structure it has much lower crystalline content and density. This results in it having a low softening point 95°C, stiffness and a greater permeability to gases. As a result it is not commonly used in boil in the bag applications.

In contrast, high density polyethylene (HDPE), has much less branching than LDPE and a higher degree of crystallinity 75-90% resulting in a stiffer polymer with a higher softening point 121°C. Its barrier properties to gases and chemical resistance; especially to

oils and greases, are also superior to LDPE by a factor of 5 for the same thickness of material. The polymer does not absorb moisture and provides good water vapour barrier properties, which makes it useful in packaging applications. HDPE was first produced in the early 1950's by Ziegler and Natta (81-82) who developed new organometallic polymerization catalysts with unique stereoregulatory properties. These enabled polymerization to be carried out at 60-70°C and at a pressure of about 7 atmospheres.

Until recently HDPE was the principal polyethylene used in food contact applications but the property gap that exists between HDPE and LDPE has been filled by linear low density polyethylene (LLDPE). It has the density of LDPE and the structure of HDPE without the need for a high pressure polymerization process. LLDPE is prepared by solution or gas phase polymerization, and is actually a copolymer of ethylene with 8-10% of an α-olefin such as but-1-ene, pent-1-ene, hex-1-ene or oct-1-ene. This produces a chain with a controlled number of short chain branches, and densities intermediate between HDPE and LDPE, thereby allowing it to be prepared in various grades by controlling the type of comonomer. In film applications LLDPE offers higher tensile strength, puncture resistance and better high temperature properties than conventional LDPE. Hence LLDPE has begun to find uses in high temperature applications previously prohibited for LDPE because of its low softening temperature.

3.1.2 Polypropylene

Polypropylene (PP) is synthesized by solution polymerization using propylene monomer under controlled conditions of heat and pressure in the presence of organometallic, stereospecific catalysts of the Ziegler Natta type. Depending on the catalyst and polymerization process used, the molecular structure of the resulting polymer consists of three different types of stereochemical configurations. These are (atactic, syndiotactic and isotactic) in varying amounts. Most commercial forms of PP are at least 95% isotactic. In isotactic PP the methyl groups are all on the same side of the polymer backbone, providing a structure with a high degree of crystallinity. The crystalline nature of the isotactic form gives it good chemical and heat resistance. It is particularly resistant against oils, greases and moisture, and its high softening point 170°C enables it to easily withstand steam sterilization.

By comparison, polyethylenes have higher densities, significantly lower melting temperatures, and a lower flexular modulus (stiffness). These property distinctions lead to

differences in end uses. Stiffness and ease of orientation makes PP suitable for numerous fibre and film applications. While their higher heat resistance and barrier properties makes them useful in autoclaveable containers and in moulded parts for household appliances, such as kettles. The one major limitation of food contact articles made from PP is temperature. At low temperatures its impact strength is reduced and it becomes brittle, and may crack. Polypropylene is also inherently less stable than polyethylenes to heat, and oxidative attack and must be stabilized with antioxidants and ultraviolet light absorbers for satisfactory processing and longevity of the fabricated product (83).

3.1.3 Additives

Polyolefins used in food contact applications in addition to the basic polymer, contain a number of non polymeric components in small amounts. It is apparent that certain of the additives, which are usually of relatively low molecular weight could be transferred from the polymer to the food during storage and heating.

Non polymeric components are present in polymers, either unavoidably as a result of the process of manufacture, or as a result of deliberate additions to the polymer, in order to improve the ease of manufacture, or to improve the final polymer properties e.g. stabilizers, slip agents and antioxidants.

3.1.3.1 Antioxidants

One of the principal additives in polyolefins are antioxidants, which are incorporated into the polymer to prevent degradation during processing and conditions of use. For film applications the polyethylene granules used must be extruded and blown requiring temperatures of around 150°C, with the obvious potential for oxidation. In addition the final film would have to be able to withstand a short exposure to temperatures of 100°C and several months at sub ambient temperatures.

Flasks and kettles are usually produced by injection moulding where the polymer granules are heated, extruded and injected into a heated mould. Temperatures in the range 150-200°C are often used with residue times in the extruder of up to 15 minutes. In comparison with films, flasks and kettles are repeat use items and therefore must be manufactured to withstand frequent exposure to elevated temperatures for much longer periods of time.

Antioxidants are used to retard the reaction of organic materials with atmospheric oxygen (autoxidation). Such reactions can cause degradation of the mechanical and aesthetic properties of polymers. The need for antioxidants depends upon the chemical composition of the polymer and the conditions of exposure. Saturated polymers for example have greater oxidative stability and therefore require relatively low concentrations of antioxidants. By incorporating antioxidants into the polymer its useful life can be extended. The extent of the large scale usage of antioxidants in polymers can be gauged from the sales of antioxidants in the USA reaching approximately $730 million in 1990 (84).

Antioxidants are designed to inhibit specific steps in the free radical chain autoxidation process. A simplified mechanism for autoxidation of an organic material (RH) is described by equations 1-9 (85).

Initiation

RH	⟶	Production of radical R•	**(Eqs. 1)**
ROOH	⟶	RO• + •OH	**(Eqs. 2)**
2ROOH	⟶	RO• + ROO• + H_2O	**(Eqs. 3)**
ROOR	⟶	2RO•	**(Eqs. 4)**

Propagation

R• + O_2	⟶	ROO•	**(Eqs. 5)**
ROO• + RH	⟶	ROOH + R•	**(Eqs. 6)**

Termination

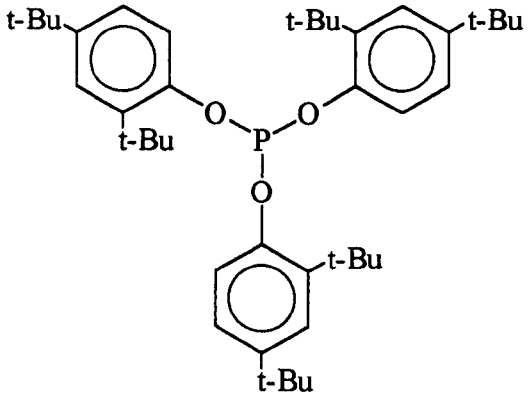
2R•	⟶	R-R	**(Eqs. 7)**
ROO• + R•	⟶	ROOR	**(Eqs. 8)**
2ROO•	⟶	ROOR + O_2	**(Eqs. 9)**

Equation 1 is important only during the very early stages of autoxidation. Radicals formed here gradually produce hydroperoxides (86) which become the kinetically important initiators. The peroxide bond is relatively weak and cleaves homolytically to yield radicals (Eqs. 2 & 3). Once oxidation has started the concentration of hydroperoxides becomes appreciable and there decomposition becomes the main source of radical initiators. One of the main causes of cleavage of the hydroperoxides, to produce radicals is by the absorption of UV light. In addition to photo-oxidation (87-92) other possible causes of early initiation steps include stress induced bond rupture; as found in polymer processing and fatigue (93-96), bimolecular reactions of hydrocarbons with oxygen (97), reaction with ozone (98), and gamma (99-100) and electron beam irradiation (101).

Autoxidation is a free radical chain reaction and therefore, can be inhibited at the initiation and propagation stages. In fact, antioxidants are often classified on the basis of their ability to do either or both. One of the main classes of antioxidants added to polyolefins to inhibit the initiation step in thermal autoxidation are peroxide decomposers, such as phosphite esters (102). These function by decomposing hydroperoxides to alcohols (Eqs. 10), thereby inhibiting initiation by equations 2 & 3.

$$(RO)_3P + ROOH \longrightarrow ROH + (RO)_3P{=}O \qquad \textbf{(Eqs. 10)}$$

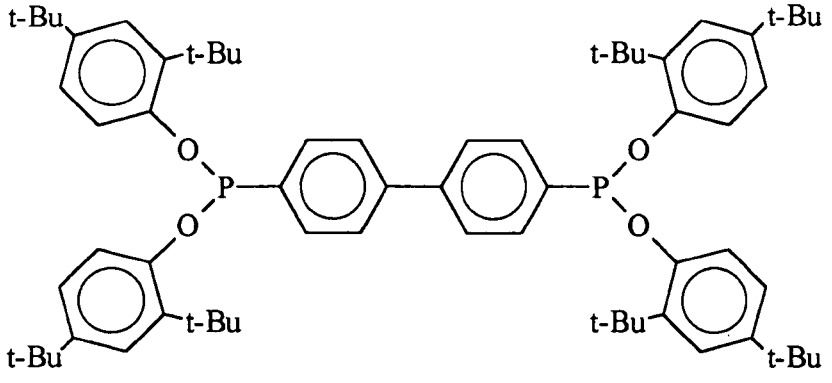
Two of the most common phosphite esters used are shown in Figures 3.1a and 3.1b.



Irgafos 168

Tris (2,4-di-tert-butylphenyl) phosphite

Figure 3.1a Phosphite ester used in polyolefins

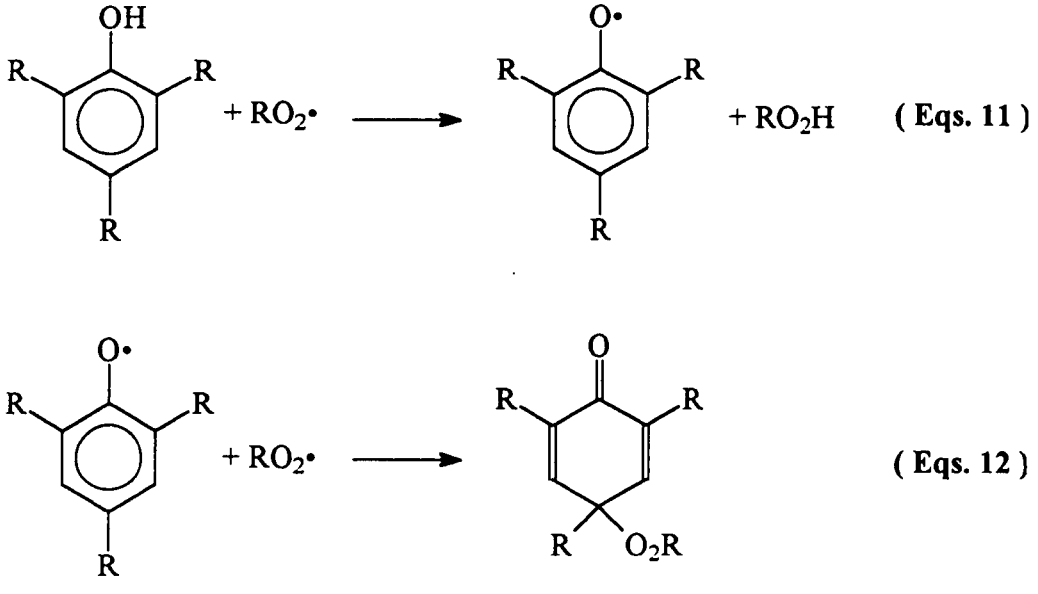


Irgafos P-EPQ

Tetrakis (2,4-di-tert-butylphenyl) 4,4'-biphenylenediphosphonite

Figure 3.1b Phosphite ester used in polyolefins

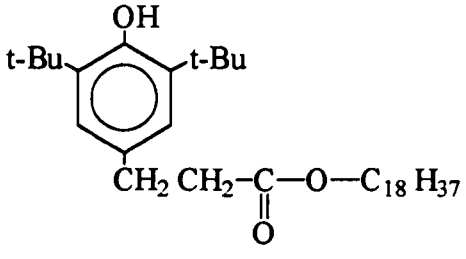
Another method of reducing the oxidation rate, is to employ an agent that interrupts the propagation step (Eqs. 6). The most important commercial antioxidants that function in this way for polyolefins are hindered phenols. The mechanism of inhibition involves hydrogen atom transfer to the peroxy radical, forming a non radical substrate (Eqs. 11). A second peroxy radical is then often trapped by adduct formation (Eqs. 12) (103-104).



Substituents on the phenolic ring have a profound affect on the activity and stability of phenolic antioxidants (105). Hindering the phenolic hydroxyl group with at least one bulky

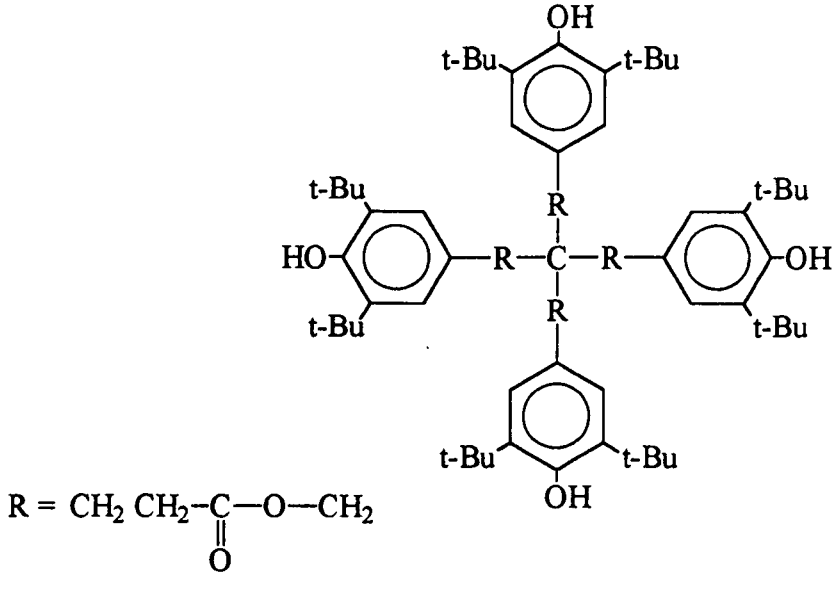
alkyl group in the ortho position appears to be necessary for high antioxidant activity. As a result nearly all commercial antioxidants are hindered in this manner. In addition steric hinderance decreases the ability of the phenoxyl radical to abstract a hydrogen atom from the substrate and thus produce an alkyl radical capable of initiating oxidation.

The usefulness of a hindered phenol for a specific application also depends on its solubility in the polymer substrate, and its volatility (106). By introducing long aliphatic chains into an antioxidant molecule these problems are overcome. A variety of such hindered phenols for use in polyolefins have been developed. Two of the most commonly used are shown in Figure 3.2.



Irganox 1076

Octadecyl -3- (3',5' -di-tert-butyl-4'-hydroxyphenyl) propionate



Irganox 1010

Pentaerythritol-tetrakis-[3,(3'-5'-di-tert-butyl- 4'-hydroxyphenyl) propionate]

Figure 3.2 Hindered phenol antioxidants used in polyolefins

Most often polymers contain a combination of certain antioxidants that provide a higher degree of protection than the sum of the stabilizing activity of each component (synergistic protection). The most common synergistic combinations are mixtures of antioxidants operating by different mechanisms, for example combinations of peroxide decomposers with propagation inhibitors are commonly used in polyolefins (107-109). These materials are compounded into the polymer typically at around the 0.1% w/w level.

3.1.4 Toxicological and legislative aspects

Monomers used in the production of polyolefins have been assessed by the Scientific Committee for Food (SCF) (110) and their present use in plastic materials intended to come into contact with foodstuffs has been deemed as acceptable. The SCF could not establish an acceptable daily intake (ADI) or tolerable daily intake (TDI) for the monomers, however, it is the opinion of the SCF that their migration into food will be toxicologically negligible. This being a direct result of the residues of these gases in the plastic being very small, and their very low toxic potential. Also according to the list of authorised monomers and other starting materials (Section A) laid down in directive 90/128/EEC (20) no specific restrictions are stated for the residual monomers in polyolefins.

The majority of toxicological work has centred around the antioxidants used in the polymer and their transformation products. The low molecular weight phenolic antioxidants 2,6-di-tert-butyl-4-methylphenol (BHT) and 2,6-di-tert-butyl-4-methoxyphenol (BHA) have been extensively covered due to their volatility, especially in polymeric materials at elevated temperatures, where their solubility in the polymer is affected. Both BHT and BHA are generally permitted for use in foods in a number of countries, including the U.S.A. and U.K. Reviews of the safety of these antioxidants (111,112) provide no consistent evidence of any significant direct toxicity in experimental animals at dose levels that are one hundred times the maximum amounts likely to be consumed by man, under the present legal limits of use. Recently, however, carcinogenic (113) and genotoxic (114) activities have been reported, and this information has been used to question the safety of these antioxidants in food. These factors have to be taken into consideration, but may be outweighed by the protective effect of BHT and BHA. Since their ability to scavenge and inactivate superoxide radicals, hydroxyl radicals, hydrogen peroxide and lipid hydroperoxides and to induce other deactivating enzymes has been reported and linked to their ability to reduce or eliminate the effects of

DNA reactive carcinogens (114-118). Both BHT and BHA have been evaluated by the SCF and have established an ADI of 0.05mg kg^{-1} and 0.5mg kg^{-1} body weight respectively (26).

Antioxidants are incorporated into the polymer to prevent degradation of the polymer during fabrication. In order to produce a film the polyolefin granules must be extruded and blown requiring temperatures of around 150°C with the obvious potential for oxidation. In the process of protecting the polymer in both the initiation and propagation steps of oxidation the antioxidants breakdown and produce a series of transformation products. The higher molecular weight hindered phenolic antioxidants Irganox 1010 and Irganox 1076 are less volatile than their smaller analogues, and the extent of transformation products produced by BHT are not observed (119). One of the major transformation products of these antioxidants is 2,6-di-tert-butyl-1,4-benzoquinone (DTBBQ). In a study carried out by Daniel et al.(120), the small amounts of DTBBQ likely to be present in foods were found to cause no biological effects other than those identified after the feeding of the parent compound. Irganox 1010 and Irganox 1076 have been assessed by the SCF (26) and a TDI of 3mg kg^{-1} body weight has been established for Irganox 1010. However, not enough toxicological data exists for Irganox 1076 for the committee to express an opinion, so no ADI or TDI has been established.

Again due to their size the volatility of Irgafos 168 and Irgafos P-EPQ incorporated into polyolefins is low, rendering inhalation hazards small. They are also relatively inert to hydrolysis due to the presence of bulky aromatic groups near the site of reaction, unlike their alkyl analogues which undergo cleavage at the C-O or P-O positions.

The toxicity of the organic phosphates varies extensively from very low to very high. In the most severe situation they have been known to cause damage to the central nervous system and paralysis (121). Although a minimum paralytic dose in man has yet to be established for organic phosphates, from the work carried out by Smith et al. (122) it can be estimated at about 10-30mg kg^{-1} body weight. However, even though toxicological data does exist for Irgafos 168 and Irgafos P-EPQ, the data is insufficient, and neither the ADI or the TDI has been established (26).

3.2 EXPERIMENTAL

The results compiled in this Section on polyolefin materials include a determination of the levels of additives in the material as supplied. These are commercial and not analytical grade materials so a variation of ± 15% in the antioxidant levels within a given batch of polyolefin would not be considered unusual. Other determinations include the overall migration characteristics of the different polymers used and an investigation of the antioxidants and their degradation products.

3.2.1 Materials

Polyolefin samples

The seven polyethylene films and two polypropylene samples used in these investigations were all of commercial quality. The sample area and thickness were carefully checked and the mass of a known area of polymer was determined for subsequent migration calculations (see Appendix 1). It should be noted that the old polyethylene samples were acquired in 1988 for the previous research project (123), and the new films from the same commercial source in 1993.

Polyethylene Film Samples

Type of Film	Old Film	New Film
15μm LLDPE	√	√
50μm LLDPE	√	√
15μm HDPE	√	√
50μm HDPE	√	

Polypropylene samples

Polypropylene flask insert for vacuum flask.

Polypropylene kettle body.

Reagents

The following reagents were used :-

Millipore water - (resistivity 18MΩ cm - milli-RO15 water system)

Napolina olive oil - purchased at retail outlet

Dow Corning 200/50 cs Silicone fluid
(BDH Laboratory Supplies, MERCK LTD, Lutterworth, Leicester, U.K.)

HPLC grade acetonitrile, HPLC grade tetrahydrofuran, and HPLC grade dichloromethane (Rathburn, Walkerburn, U.K.)

30% w/v Hydrogen peroxide
70% tert-butyl-hydroperoxide
3,5-di-tert-butylphenol **(3,5-DTBP)**
2,4-di-tert-butylphenol **(2,4-DTBP)**
2,6-di-tert-butylphenol **(2,6-DTBP)**
2,6-di-tert-butyl-1,4-benzoquinone **(2,6-DTBBQ)**
2,6-di-tert-butyl-4-methylphenol **(BHT)**
2,4,6-tri-tert-butylphenol **(2,4,6-TTBP)**
(Aldrich Chemical Company, Gillingham, Dorset, U.K.)

The commercial antioxidants Irganox 1010, Irganox 1076, Irganox 1330 (1,3,5-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)-2,4,6-trimethylbenzene), Irgafos 168 and Irgafos P-EPQ were supplied by Ciba-Geigy Additives, Hulley road, Macclesfield, Cheshire, U.K.

3.2.2 Analysis of polyolefin antioxidants

As previously stated in Section 3.1.3.1 polyolefins are sensitive to thermal and photo-oxidative degradation. Consequently a range of antioxidants and light stabilizers are employed to improve the useful properties and to extend the service life of polyolefins. From the analytical point of view two main problems are encountered with the analysis of these additives:- i) Extraction of the additives from the polymer matrix and

ii) Identification and quantification of low concentrations of additives.

The difficulties involved in extraction of additives have resulted in a search for analytical techniques not involving prior separation of the antioxidants from the polymer. In situ spectroscopic methods such as ultraviolet absorption, infrared, fluorescence or phosphorescence and X-ray fluorescence (124-125) have all been used, but these methods generally lack specificity. This can be overcome by the use of dynamic headspace sampling (126) and pyrolysis mass spectroscopy (127-130), but limitations on volatility and degradation of high molecular weight antioxidants at elevated temperatures limit the usefulness of these techniques.

In view of the limitations of 'in situ' analysis some form of preliminary separation of the antioxidant from the polymer is necessary. Most of the separations reported (131) are concerned with solid / liquid extraction, since the insoluble nature of the polymer matrix precludes the possibility of using the more efficient liquid / liquid extraction.

Polyolefins are the most difficult type of polymer to analyse, because of their insolubility. Various methods have been reported involving the dissolution of the polymer in boiling toluene (132-133), and extraction with ultrasonic baths and microwave ovens (134-135). However, problems with sample loss, and increased rate of stabilizer decomposition at the high temperatures involved make these extraction methods unsuitable. Other techniques used to extract antioxidants from polyolefins include soxhlet extraction (125) and supercritical fluid extraction [SFE] (136-139). Both techniques, under the correct conditions, are less likely to lead to stabilizer degradation. The only limitation of soxhlet extraction is that several hours are necessary for complete extraction, whereas SFE requires only a few minutes.

Almost all polyolefin types contain mixtures of stabilizers. All polyolefins have to contain at least one antioxidant but, usually, two or more different antioxidants are employed

(synergistic mixtures). Consequently in most cases the separation and detection of each stabilizer of the additive package is necessary.

Nuclear magnetic resonance spectroscopy (NMR) (140) has been employed to quantify a range of antioxidants in a toluene extract of LDPE. Although suitable, errors in quantification were large due to the inability of NMR to discriminate between a mixture of antioxidants in the sample. In order to separate the range of stabilizers in the polyolefin extract some form of chromatographic technique is required. Paper and thin layer chromatography (125,126,141,142) have been used with various detection methods to identify the separated fractions, but their analytical performance has been superseded by modern column chromatography.

Several workers have reported the use of gas chromatography (GC) for the analysis of antioxidants (143-150). Whilst suitable for the simultaneous separation and identification of small quantities of complex mixtures it is limited by the low volatility of the higher molecular weight antioxidants. To overcome this problem the non-volatile components have been converted into more volatile components by saponification with potassium hydroxide (151) and transesterification with methyl alcohol (152). However, the formation of derivatives before chromatography often leads to sample loss and the appearance of spurious peaks.

In comparison with the above methods, the introduction of gel permeation [GPC] (153-159), high performance liquid [HPLC] (160-171) and supercritical fluid chromatography [SFC] (136-139,172-174) have enabled the quantitative separation of these underivatised high molecular weight stabilizers. Although gel permeation chromatography is a simple analytical method it suffers two main disadvantages: very poor resolution, and low sensitivity. For complex stabilizer mixtures HPLC and SFC appear to be the most suitable chromatographic techniques with appreciable improvements in analysis time and component separation. In order to identify compounds present in commercial samples comparisons of peak retention times or capacity factors (k') with those of known standards has to be made. Identification by this method is not only time consuming and tedious but requires all the suspected compounds to be at hand. The combination of gas chromatography with mass spectrometric detection (GC-MS) can circumvent many of these problems, but is limited to additives that are volatile (175). To overcome this problem a variety of other MS techniques including laser desorption, fast atom bombardment (176) and time of flight secondary ion mass spectrometry (177) have been used. In recent years several workers have utilized the direct coupling of a liquid chromatograph to a mass spectrometer (LC-MS) to analyse

thermally unstable and high molecular weight polymer additives. A number of interfaces have been developed including moving belt (178) and particle beam (179,180); both have been used to characterise transformation products from high molecular weight hindered phenols in polypropylene samples subjected to ionizing radiation.

3.2.3 Quantification of initial antioxidant levels in polyolefins

In this investigation samples of the polyethylene and polypropylene materials were quantitatively soxhlet extracted with acetonitrile and the resultant levels of the various antioxidants in the extracts were determined by HPLC using Irganox 1330 as the internal standard.

The first step in the analysis was the determination of the most suitable wavelength for the range of antioxidants under investigation. Yagoubi et al. (169) determined the limit of sensitivity of several antioxidants utilizing UV, electrochemical and light scattering diffusion detectors in conjunction with HPLC. He determined that electrochemical detectors were the most sensitive followed closely by UV, monitoring at 280nm. In most of the HPLC analyses carried out on antioxidants UV detectors were utilized monitoring at 280nm with gradient elution (162,163). Gradient elution enables the percentage of two or more solvents used in the eluent to be changed during the analysis, and therefore shortens the analysis time. The limitation of gradient elution is that it precludes the use of shorter wavelengths due to the zero absorbance shifting as the eluent composition changes. However, by using isocratic conditions and suitable solvents monitoring can be carried out at shorter wavelengths.

Figure 3.3 compares the absorbance at 230 and 280nm for a range of antioxidants dissolved in acetonitrile to the same concentration, and monitored in a Perkin Elmer 554 UV/VIS spectrometer scanning over the range 180-400nm.

From the subsequent spectra obtained 230nm was determined to be the optimum wavelength for the range of antioxidants being investigated. The shorter wavelength having an absorbance that was three to four times greater than at 280nm. Wavelengths less than 230nm showed stronger absorbance, but interference from the acetonitrile employed as the eluent for the HPLC precluded its use.

On determining the most suitable wavelength to use it was then possible to quantify the initial levels of antioxidant in polyethylene and polypropylene samples. Polyolefin samples of accurately known mass were chopped into 1cm squares and soxhlet extracted for a minimum of 24 hours using 150cm^3 of acetonitrile. The acetonitrile was then removed and

analysed using the chromatographic conditions cited below in Table 3.1, employing Irganox 1330 as an internal standard.

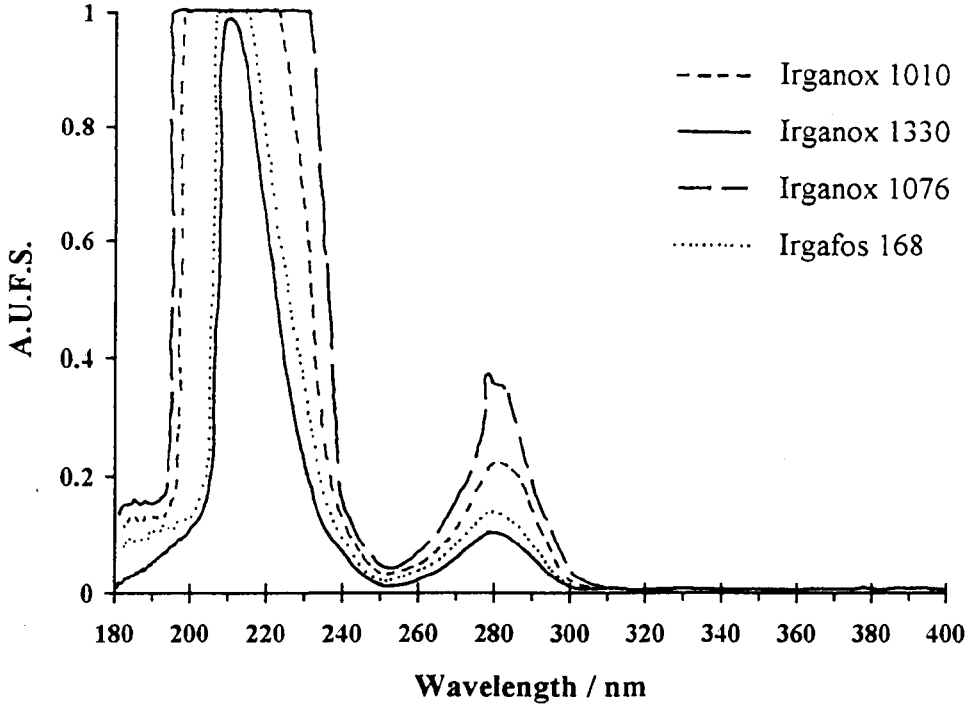


Figure 3.3 Comparison of absorbance of antioxidants

Eluent	:	100% Acetonitrile
Flow rate	:	1.5cm^3 min^{-1}
Pump	:	Pye Unicam PU4015
Injector	:	Marathon Autosampler 100µl sample loop at 30°C
Column	:	Alphasil 5µm ODS C_{18} 250 x 4.6mm i.d. HPLC Technology Ltd. Macclesfield, UK.
Detector	:	ACS Model 750/11/AZ UV at 230nm
Integrator	:	Hewlett Packard HP3394A

Table 3.1 Summary of HPLC experimental conditions

The antioxidant levels in the film were determined using the following equations based on internal standard calibration methods.

$$\text{Concentration of antioxidants } (\mu g\ dm^{-2}) = \frac{C_{ISTD} \times A_{SPL} \times CF \times 150{,}000}{A_{ISTD} \times A_{PO}}$$

$$\text{Concentration of antioxidants } (\mu g\ g^{-1}) = \frac{C_{ISTD} \times A_{SPL} \times CF \times 150{,}000}{A_{ISTD} \times M_{PO}}$$

Where :-

A_{SPL} = Peak area of antioxidant peak

A_{ISTD} = Peak area of Irganox 1330 used as internal standard

C_{ISTD} = Concentration (mg cm^{-3}) of Irganox 1330 used as internal standard

A_{PO} = Area (dm^2) of polyolefin in contact with food simulant

M_{PO} = Mass (g) of polyolefin sample extracted

CF = Correction factor at 230nm for specific antioxidants

The individual correction factors have been determined from the calibration plots shown in Figure 3.4, and are shown in Table 3.2.

$$\text{where CF} = \frac{\text{Change in peak area of Irganox 1330 per mg } dm^{-3}}{\text{Change in peak area of antioxidant per mg } dm^{-3}}$$

Antioxidant	Response Factor
Irganox 1010	3.17
Irganox 1330	1.00
Irganox 1076	5.47
Irgafos 168	1.34

Table 3.2 Response factors for individual antioxidants

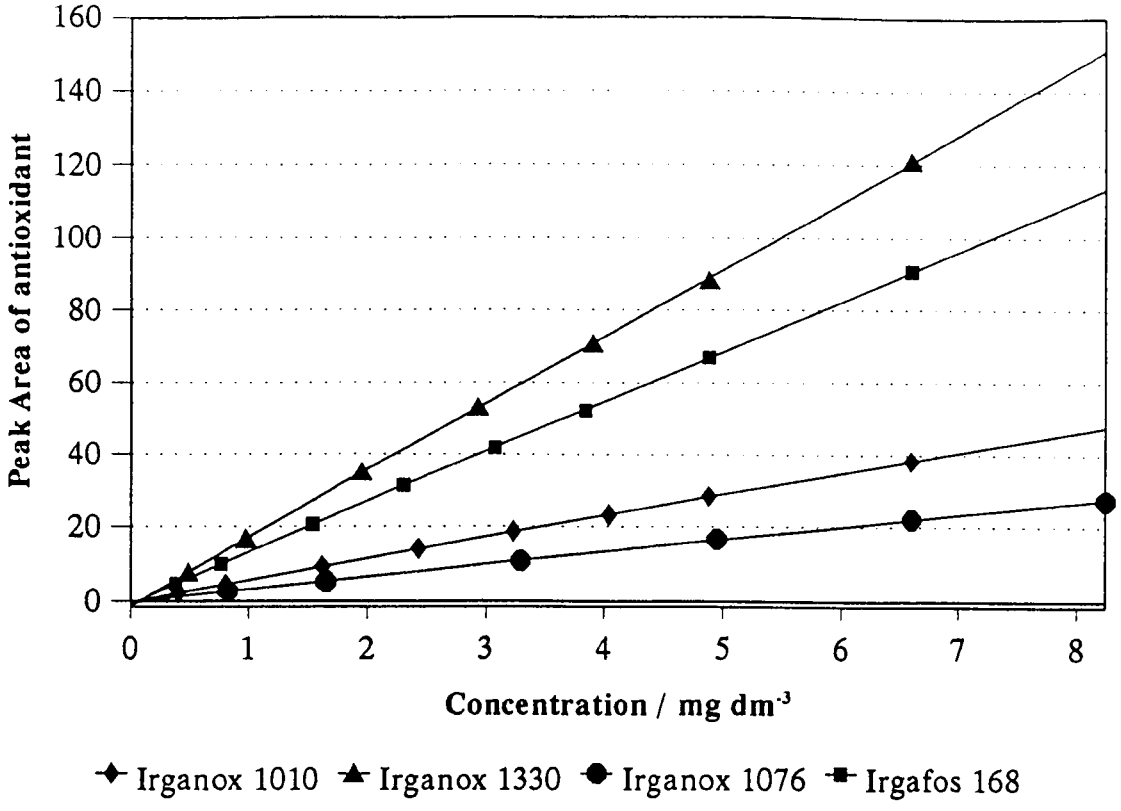


Figure 3.4 Calibration plots of antioxidants

These analyses were carried out to quantitatively determine the levels of antioxidants present in the polyolefin samples; which may migrate into a food simulant, and to compare the detected with the stated levels supplied by the manufacturer. Irgafos P-EPQ could not be analysed as a single species since the material is really the mixed products resulting from the reaction of di-tert-butyl-phosphonite with biphenyl, obtained by condensation of 2,4 di-tert-butylphenol with the Friedel Craft reaction product of phosphorous trichloride and biphenyl (181). The product as sold, contains around 12% Irgafos 168 as an impurity (182). The results in Table 3.3 therefore compare the measured levels of antioxidants with those specified (indicated by []) for Irganox 1010, Irganox 1076, Irgafos 168 and Irgafos P-EPQ.

Levels of antioxidants detected in the new films were similar to those stated by the manufacturer inferring that little antioxidant degradation had occurred due to the processing or polymer ageing. However, Irgafos 168 was detected in the LLDPE samples, which was a result of the incorporation of P-EPQ into the polymer matrix. In comparison with the new film data the amounts of residual antioxidants in the old films; apart from Irganox 1076, have been reduced. In addition, no Irgafos 168 could be detected even though Irgafos P-EPQ was

incorporated into the polymer, implying that the Irgafos 168 has undergone degradation to the coresponding phosphate (see Section 3.1.3.1).

This information is presented in an alternative form in Table 3.4 where the levels of antioxidants extracted per dm^2 of material in contact with the solvent has been calculated.

3.2.4 Investigation of overall migration from polyolefins

The migration experiments were based on a 60 minute immersion of the test specimen into boiling 18MΩ millipore water or oil at 100°C. Where the pouch was used the food simulant was at ambient temperature prior to immersion. Conventional total immersion tests, single sided cell and pouch tests were used as convenient, and for comparison purposes (123,76). Sample sizes ranged from 20 x 10cm for the total immersion tests, to 20 x 20cm for the pouch tests. Pouches were prepared using a Hulme Martin dual electronic sealer where commercial samples were not available.

For overall migration determinations using an aqueous simulant the millipore water was removed from contact with the polyolefin film after 60 minutes and transferred to a stainless steel crucible. The water within the crucible was slowly evaporated off and the crucible and its contents dried until a constant mass was obtained. With oil simulants the mass loss on the test specimens are not so simple to determine and the standard CEN methodology was employed (183,184).

The results obtained from similar materials from different commercial sources have been compiled in Table 3.5. To prevent repetition of work carried out on polyethylene films the oil simulant data was abstracted from results compiled by Mulroy (123). These results are derived from different materials and several different test methods so it is appropriate therefore to cite only the range of migration results obtained. The data for the polypropylene sheet (flask and kettle bodies) was obtained from total immersion tests and due attention was paid to inclusion of the extra surface area resulting from any edge effects.

In all cases the results cited in Table 3.5 are based on replicate analyses of several different samples from at least two different commercial sources. As can be seen these migration values are generally below the specified maximum of 10mg dm^{-2}. Levels migrating into the aqueous food simulant were found to be significantly less than those for oil simulants, due to the ability of the oil to penetrate into the polyolefin and act as a plasticizer. The anomalously high value observed for the 50μm LLDPE in an oil simulant resulted from high levels of calcium stearate incorporated into the film (123).

Polyolefin Sample	Antioxidant level / μg g^{-1}			
	Irganox 1010	**Irganox 1076**	**Irgafos 168**	**Irgafos P-EPQ**
NEW LLDPE FILMS				
15μm	230 ± 20 [300]	ND [NI]	120 ± 10[a] [0]	960[b] [800]
50μm	230 ± 10 [300]	ND [NI]	120 ± 5[a] [0]	960[b] [800]
NEW HDPE FILM				
15μm	120 ± 5 [300]	ND [NI]	1100 ± 100 [1000]	600 [500]
OLD LLDPE FILMS				
15μm	ND [200]	ND [NI]	180 ± 20 [800]	ND [NI]
50μm	5 ± 1 [200]	ND [NI]	300 ± 20 [800]	ND [NI]
OLD HDPE FILMS				
15μm	ND [NI]	1050 ± 50 [900]	ND [0]	[c] [500]
50μm	ND [NI]	1100 ± 50 [900]	ND [0]	[c] [500]
POLYPROPYLENE	200 ± 20 [*]	ND [*]	240 ± 20 [*]	ND [*]

[a] Irgafos 168 was identified as a contaminant present in Irgafos P-EPQ

[b] P-EPQ cannot be quantified by these HPLC conditions; the level cited is determined from the data for Irgafos 168 assuming a 12% level in P-EPQ

[c] P-EPQ cannot be quantified by these HPLC conditions; unable to determine level from Irgafos 168 data

ND Not detected

NI Material not incorporated into the polymer

* No data available

Table 3.3 Measured and specified [ ] antioxidant levels for various polyolefin materials

Polyolefin Sample	Amount / μg dm^{-2}			
	Irganox 1010	**Irganox 1076**	**Irgafos 168**	**Irgafos P-EPQ**
NEW LLDPE FILMS				
15μm	40 ± 5	NI	20 ± 5[a]	140[b]
50μm	100 ± 10	NI	50 ± 10[a]	500[b]
NEW HDPE FILM				
15μm	20 ± 5	NI	160 ± 20	100[b]
OLD LLDPE FILMS				
15μm	ND	NI	36 ± 4	NI
50μm	2 ± 0.5	NI	130 ± 10	NI
OLD HDPE FILMS				
15μm	NI	75 ± 5	ND	[c]
50μm	NI	240 ± 10	ND	[c]
POLYPROPYLENE	2000 ± 200	ND	2500 ± 200	ND

[a] Irgafos 168 was identified as a contaminant present in Irgafos P-EPQ

[b] P-EPQ cannot be quantified by these HPLC conditions; the level cited is determined from the data for Irgafos 168 assuming a 12% level in P-EPQ

[c] P-EPQ cannot be quantified by these HPLC conditions; unable to determine level from Irgafos 168 data

ND Not detected

NI Material not incorporated into the polymer

Table 3.4 Antioxidant levels in polyolefins expressed as mass / unit area in contact with solvent

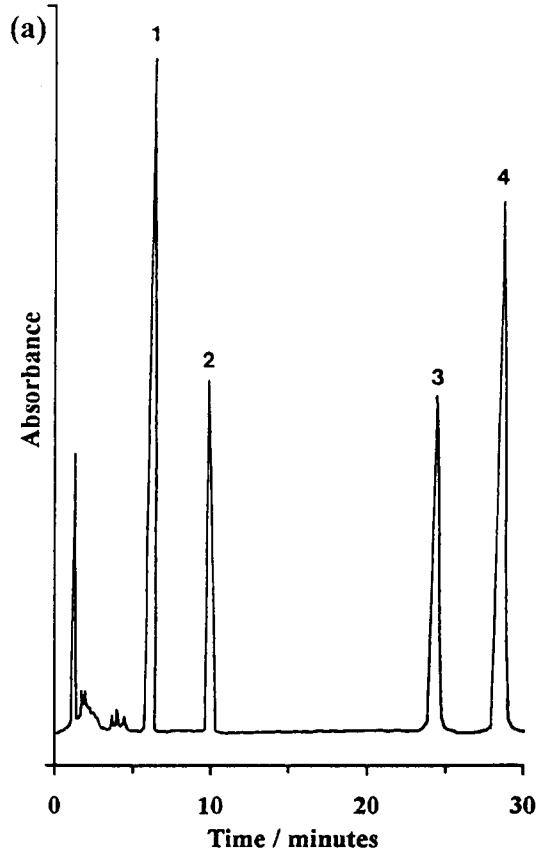
Sample	Overall migration / mg dm^{-2}	
	Aqueous simulant	Oil Simulant
Films		
15μm HDPE	< 0.1	2.2 - 4.6
50μm HDPE	< 0.1	2.1 - 3.0
15μm LLDPE	< 0.1	1.4 - 6.7
50μm LLDPE	≤ 0.1	4.2 - 18.5
Utensils		
Polypropylene		
Kettle	0.5	3.5 - 6.7
Flask	0.6	4.0 - 7.2

Table 3.5 Overall migration data

3.2.5 Quantification of antioxidants migrating from polyolefins

Gravimetric measurement is a suitable technique for obtaining an overall migration value for the total amount of material migrating from a polyolefin into an aqueous and oil food simulant. However, it is unable to identify and quantify the individual species migrating from the polyolefin samples. In order to do this the food simulant after the migration period must be subjected to either chromatographic or spectroscopic analysis, or both to identify and hence quantify the species present.

In Section 3.2.3 several antioxidants were identified as being present in the polyolefin samples. In this investigation the same HPLC conditions with UV detection were employed to determine if any of these antioxidants had migrated into food simulants. Such analyses can be readily achieved when millipore water is the simulant, but attempts to analyse olive oil spiked with antioxidants (Figure 3.5b) have shown the presence of levels of contaminants in the olive oil which would obscure those resulting from compounds migrating from the polymer. Indyk et al. (185) have identified some of these extractables from edible oils and fats to be antioxidants. Even after multiple extractions with suitable solvents to clean the oil samples up the small amounts of species migrating from the polymer samples into the oil where indistinguishable from the background interference of blank oil.

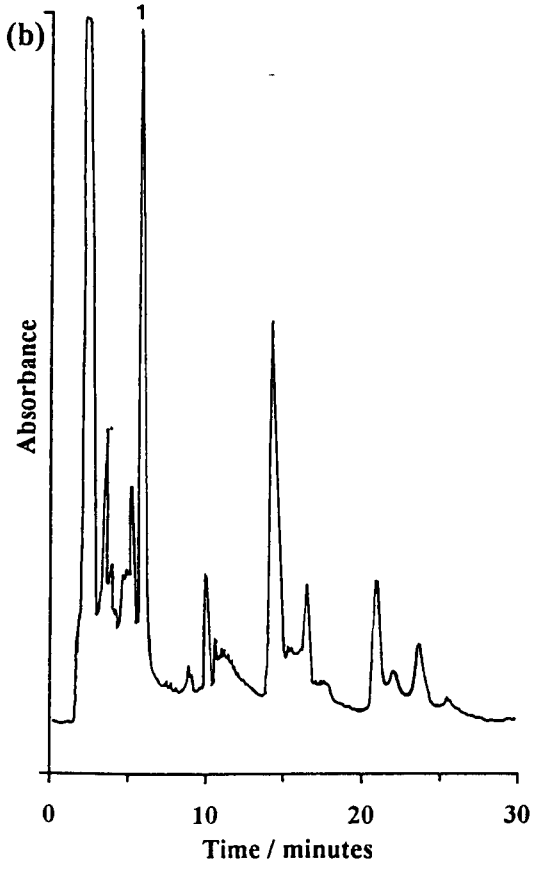


1 = Irganox 1010

2 = Irganox 1330 (I.S.)

3 = Irganox 1076

4 = Irgafos 168



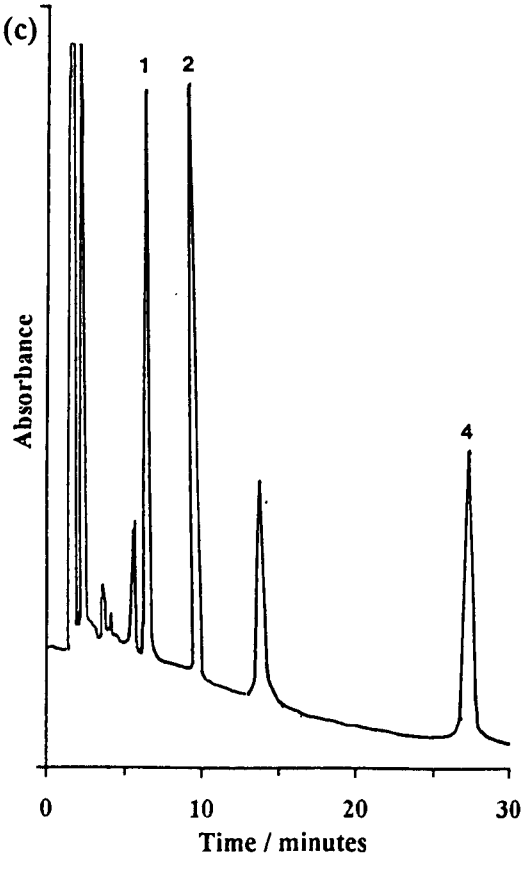


Figure 3.5 **Comparison of HPLC traces for antioxidants from :-**

a) Aqueous simulant b) Olive oil c) Silicone oil

Using silicone oil in place of olive oil produces an almost ideal analytical system where no interference is detected from the silicone oil, and the results can be readily interpreted as shown in Figure 3.5c.

The film samples provide a simple case where the migration data can be obtained from either total immersion or pouch samples which are discarded after each experiment. In these experiments it is only necessary to ensure the correct value for the surface area is used in the final calculation. The flask and kettle samples are repeat use items however and multiple migration studies were therefore carried out.

Sample preparation for aqueous and oil simulants

Polyolefin samples of known mass and area were chopped into 1cm squares prior to total immersion for one hour in 18MΩ millipore water or silicone oil at 100°C. The aqueous food simulants were then rotary evaporated to dryness under an atmosphere of nitrogen and the residue was redissolved in $10cm^3$ of acetonitrile prior to HPLC analysis (Table 3.1). Levels of antioxidants migrating being determined by employing external standard calibration methods.

The silicone oil samples were extracted using two $25cm^3$ aliquots of acetonitrile in accordance with previously determined recovery data for spiked oil samples (Section 7.3). The combined extracts were then analysed by HPLC as detailed in Section 3.2.3 employing Irganox 1330 as an internal standard.

The migration data from the films is summarised in Table 3.6 for the simulants employed. The results of this study show that high molecular weight antioxidants such as Irganox 1010 and Irgafos 168 migrate from the polyolefin samples into silicone oil. At comparable temperatures and times, the percentage of available antioxidant (Table 3.4) migrating from the different classes of polymer into silicone oil in general decreases in the order LLDPE > HDPE > PP. For example with the 50μm LLDPE film, 45μg dm^{-2} out of an available 100μg dm^{-2} of Irganox 1010 has migrated into the silicone oil (45% w/w), compared to 18μg dm^{-2} for the polypropylene flask sample out of an available 2000μg dm^{-2} of Irganox 1010 (0.9% w/w). However it should be noted that these results are in some part related to the thickness of the sample used and the morphology of the polymer. It was also found that much less migration occurred when an aqueous food simulant was used. Levels of

Irganox 1010 were found to be smaller and no Irgafos 168 was detected. These results are influenced by the ability of the food simulant to penetrate the polyolefin and modify the local environment for antioxidant mobility, and the solubility of the antioxidant in the food simulant.

Sample	Amount / μg dm^{-2}	
	Irganox 1010	Irgafos 168
WATER		
New LLDPE films		
15μm	0.7	ND
50μm	0.4	ND
New HDPE films		
15μm	<0.1	ND
Polypropylene		
Flask	0.6	ND
SILICONE OIL		
New LLDPE films		
15μm	17.0	10.0
50μm	45.0	27.0
New HDPE films		
15μm	5.0	44.0
Polypropylene		
Flask	18.0	54.0

Results are subject to a ± 10% variation

ND = Not Detected

Table 3.6 Migration of antioxidants from selected polyolefin samples into food simulants after one hour at 100°C

Table 3.7 records the results from multiple migration experiments, using an aqueous food simulant, for the chopped flask and kettle samples. In this instance the exposure experiments involved the addition of boiling water to the polymer in a round bottomed flask equipped with a condenser. The water and plastic were boiled for one hour and then the water was removed and the plastic allowed to cool for 10 minutes before the process was repeated until the flask material had been immersed in boiling water for a total of ten hours. Each aqueous sample was then rotary evaporated to dryness under an atmosphere of nitrogen and the reside was redissolved in $10cm^3$ of acetonitrile prior to HPLC analysis (Table 3.1).

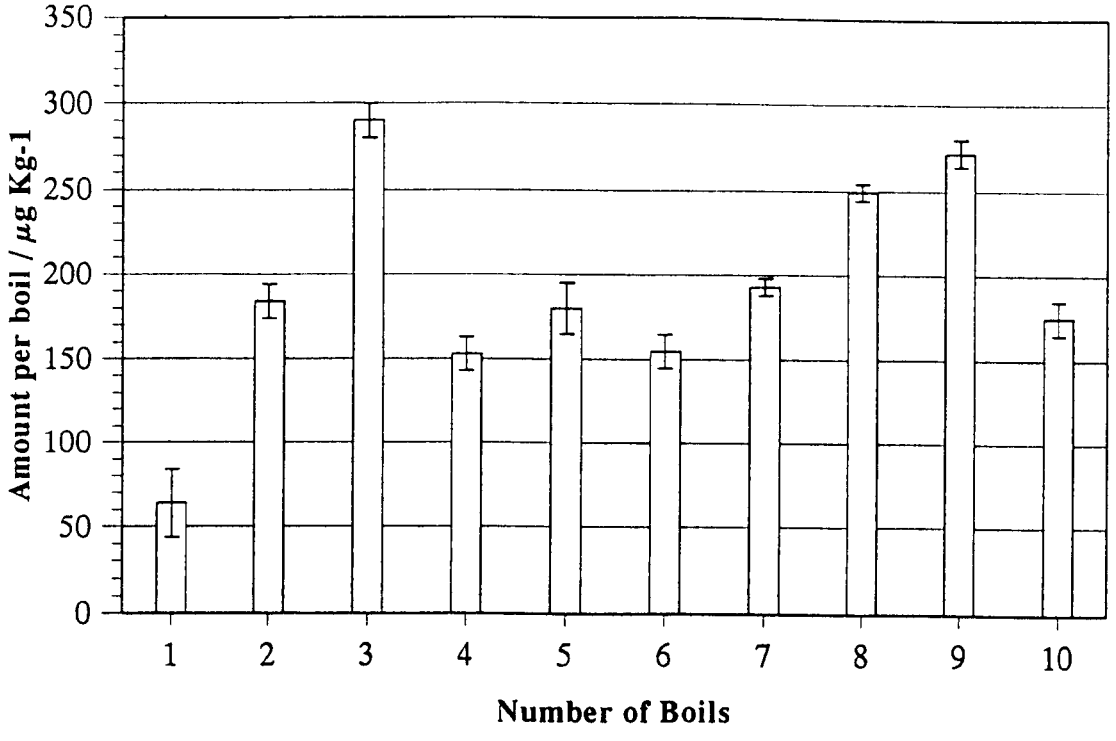
Exposure Experiment Number	Yield of Irganox 1010		Cumulative Yield of Irganox 1010	
	/ $\mu g\ kg^{-1}$	/ $\mu g\ dm^{-2}$	/ $\mu g\ kg^{-1}$	/ $\mu g\ dm^{-2}$
1	64	0.6	64	0.6
2	184	1.8	248	2.5
3	290	2.9	538	5.4
4	153	1.5	691	6.9
5	180	1.8	871	8.7
6	155	1.6	1026	10.3
7	193	1.9	1219	12.2
8	249	2.5	1468	14.7
9	272	2.7	1740	17.4
10	175	1.8	1915	19.2

Results are subject to a ± 10% variation

Table 3.7 Migration of Irganox 1010 from polypropylene into an aqueous food simulant as a function of multiple exposures

These results are compared diagrammatically in Figure 3.6 which demonstrates an increase in the yield of antioxidants for each boil up to and including the third. This can be rationalised on the basis of the loss by degradation of the surface levels of antioxidant during the production process. The higher levels of Irganox 1010 detected on subsequent migration experiments represent a return to the anticipated equilibrium values (186). After a time period of ten hours total immersion in boiling water there was no appreciable decrease in the amount of Irganox 1010 migrating during each experiment, and the anticipated decrease in these levels has not been detected.

a)



b)

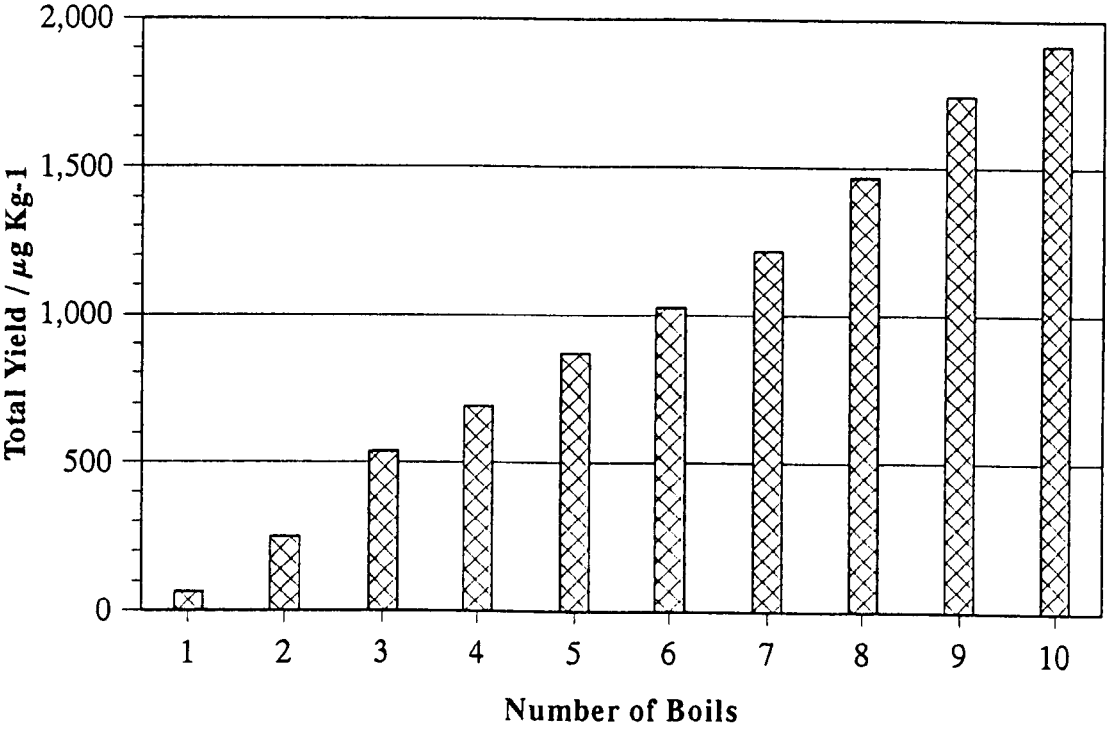


Figure 3.6 **Graphical representation of Irganox 1010 migration data for polypropylene (kettle/flask body)**

a) Individual migration per exposure

b) Cumulative migration per exposure

3.2.6 Scanning UV determinations

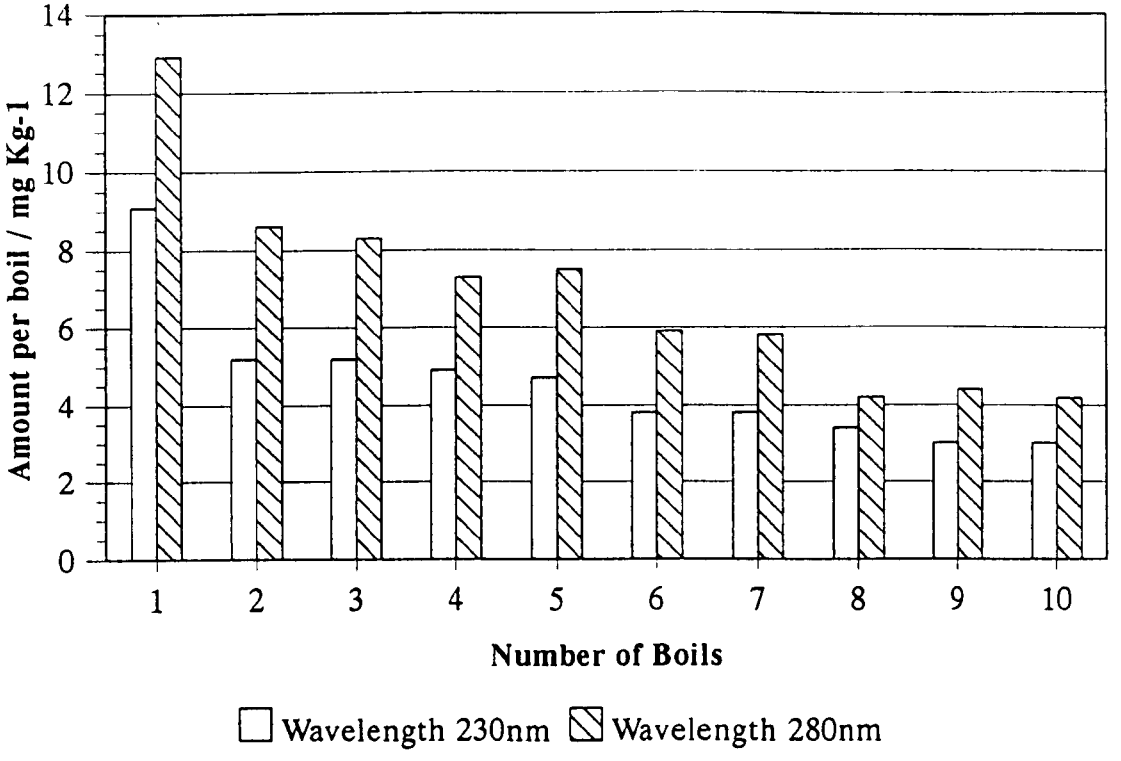
An attempt was made to correlate the results from the UV analysis of the HPLC separated antioxidants with the conventional UV absorbance of the original aqueous simulant immediately after the migration experiment. The unconcentrated aqueous samples were analysed employing the following instrumental parameters.

INSTRUMENT	:	Spectra Physics 800 UV/VIS Spectrophotometer
CELL	:	40mm path length [Quartz]
SCAN RANGE	:	200-300nm

As previously mentioned in Section 3.2.3 calibration solutions of Irganox 1010 were found to have absorption maxima at 230nm, but other workers had reported monitoring at 280nm (161-163, 169). So absorbances from the two wavelengths were used to monitor the aqueous simulants from the polypropylene. Linear calibration plots at both wavelengths over the range 0 -10 mg dm^{-3} were prepared. The absorbance figures for the aqueous samples were related to those for the Irganox 1010 calibration data to provide a migration value. The migration experiments were conducted as detailed earlier in Section 3.2.5 except that the cold aqueous solutions were subjected to UV analysis after filtration.

These results show (Figure 3.7) a steady decrease in the total UV absorbing material which migrates per boil, and also indicate that a detectable amount of UV absorbing material, 3 - 4mg kg^{-1} is migrating even after 10 hours contact with boiling water. These results are not incompatible with those in HPLC analyses where an initial increase in Irganox 1010 was observed, since these results are monitoring the total level of UV absorbing material, which includes antioxidants and all degradation products. It is suggested that the initial high levels of UV absorbing material are a result of the antioxidant degradation products and other processing aids present on the surface of the polypropylene after their production. Eventually the amounts of these materials decrease after removal from successive boils and get replaced by the migration of residual antioxidants in the polymer. Furthermore both HPLC and UV data agree on migration reaching a steady level after around 5 hours exposure at 100°C as the amounts of antioxidants migrating into the water reaches an equilibrium. It is not impossible therefore that some simplified UV analytical approach may be developed to monitor migration. The difference in the measured migration levels between the UV and the HPLC methods can be appreciated from Figure 3.8 where the Irganox 1010 peak is a very small fraction of the total peak area of the trace.

a)



b)

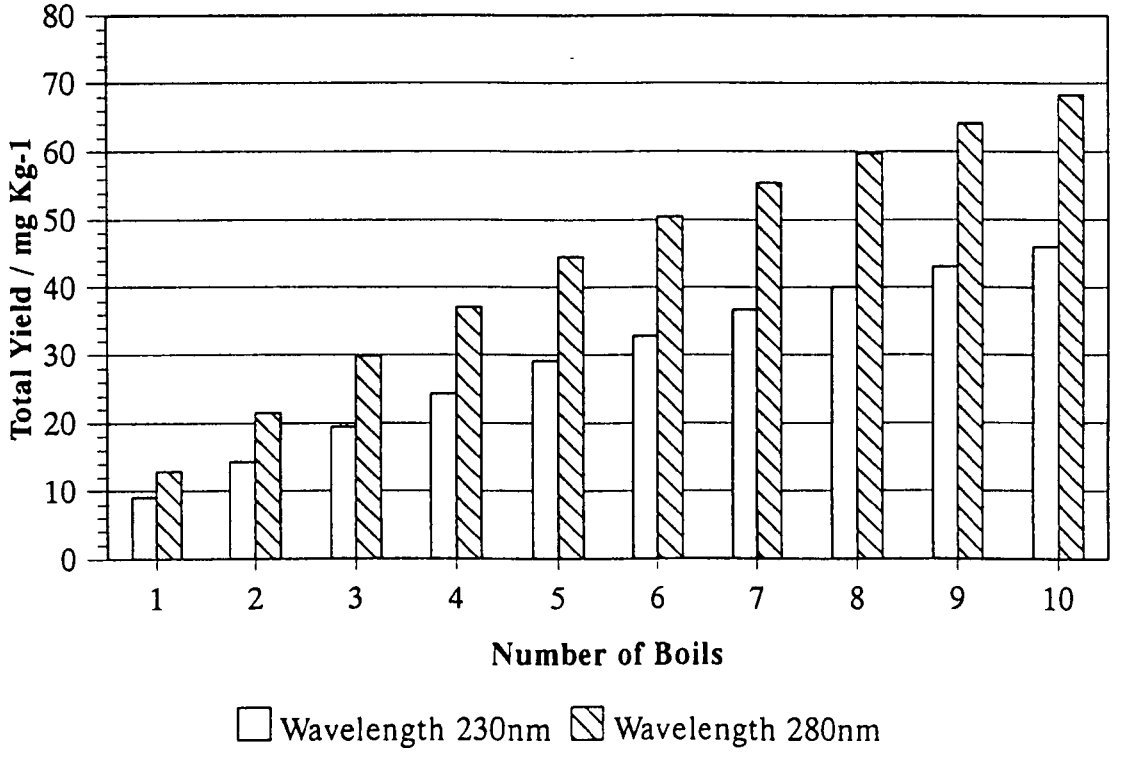


Figure 3.7 **UV analysis of total migrants into water from polypropylene (kettle/flask body) as a function of use**

a) per individual exposure b) cumulative yield

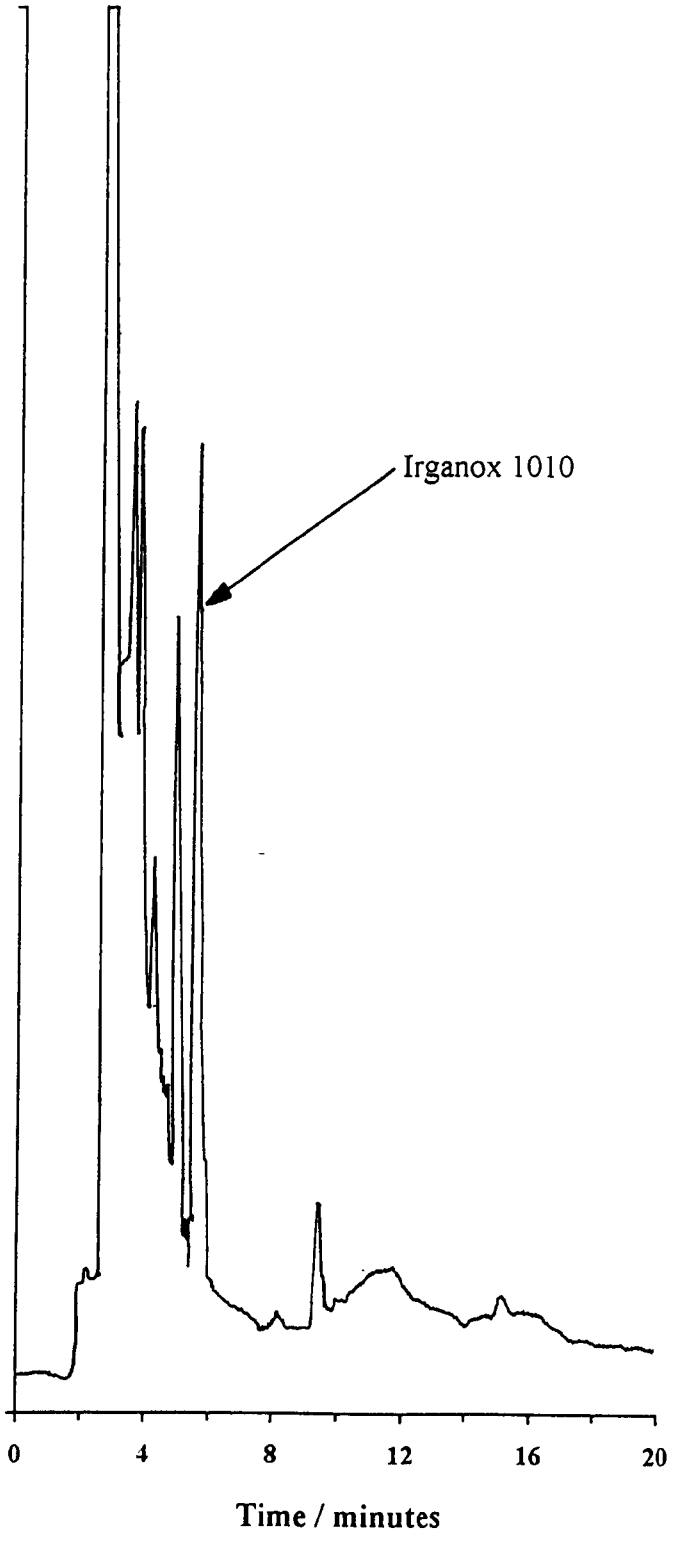


Figure 3.8 **HPLC analysis of antioxidants. Trace demonstrates the large number of UV absorbing peaks in comparison with the identified Irganox 1010.**

3.2.7 Investigation of antioxidant degradation products migrating from polyolefis

Antioxidants are incorporated into polyolefins to prevent autoxidation (Section 3.1.3.1) and by so doing, are themselves subjected to degradation. Over the years accelerated degradation of polyolefin antioxidants by thermo-oxidative (187-188) and irradiation techniques (179,180,189-192) has been investigated. Thermo-oxidative degradation of substituted antioxidants would be expected to yield a range of compounds (93, 103, 104) including :-

3,5-di-tert-butylphenol	**(3,5-DTBP)**
2,4-di-tert-butylphenol	**(2,4-DTBP)**
2,6-di-tert-butylphenol	**(2,6-DTBP)**
2,6-di-tert-butyl-1,4-benzoquinone	**(2,6-DTBBQ)**
2,6-di-tert-butyl-4-methylphenol	**(BHT)**
2,4,6-tri-tert-butylphenol	**(2,4,6-TTBP)**

It was therefore important to determine if such compounds could be formed during the simulation experiments being carried out and furthermore whether such materials were present in the polymer samples prior to experimentation. Authentic compounds were obtained from Aldrich Chemicals Company and suitable HPLC and GC-MS analytical methods were developed to produce an acceptable separation (Table 3.8 & 3.9).

Eluent	:	*Polar analytes* *Non polar analytes*	:- 80 : 20 Acetonitrile / Water :- 100% Acetonitrile
Flow rate	:	$1.5cm^3\ min^{-1}$	
Pump	:	Pye Unicam PU4015	
Injector	:	Marathon Autosampler 100µl sample loop at 30°C	
Column	:	Alphasil 5µm ODS C_{18} 250 x 4.6mm i.d. HPLC Technology Ltd. Macclesfield, UK.	
Detector	:	ACS Model 750/11/AZ UV at 230nm	
Integrator	:	Hewlett Packard HP3394A	

Table 3.8 Summary of HPLC experimental conditions for the analysis of antioxidants and their degradation products

Instrument

GC	:	Hewlett Packard 5890
MS	:	VG TRIO 3

GC Conditions

Column	:	10m x 0.32mm CP SIL - 8CB 12μm film
Carrier Gas	:	Helium 1cm^3 min^{-1}
Split	:	20 : 1
Oven programme	:	100°C to 320°C at 20°C min^{-1} hold for 5 min
Injector temperature	:	270°C

MS Conditions

Mass Range	:	30 - 700
Repeat rate	:	1 scan s^{-1}
Data handling	:	VG/PDP11 system

Table 3.9 Summary of experimental conditions for gas chromatography-mass spectrometry (GC-MS) analysis of antioxidant degradation products

3.2.7.1 Identification of antioxidant degradation products in boiling water

The thermal stability and hydrolytic degradation of BHT, Irganox 1010, 1076, Irgafos 168, P-EPQ in an aqueous environment was investigated by refluxing 5g of each antioxidant separately in 100cm^3 of boiling 18MΩ water for 4 hours. After cooling and filtering, the aqueous filtrate and solid filter residue were analysed for the presence of degradation products. The aqueous filtrate could not be analysed directly by GC-MS. So a 50cm^3 portion of the aqueous sample was extracted with five 10cm^3 aliquots of dichloromethane, which were then pooled prior to analysis.

The results showed that BHT, Irganox 1010 and Irganox 1076 did not degrade upon boiling for four hours in water. However, a significant number of impurities were found in the Irganox 1010 standard including several of the materials under investigation: 3,5-DTBP, 2,4-DTBP and 2,6-DTBBQ. The aqueous filtrate solutions all contain about 0.1% w/v of the original antioxidant material and the solutions for BHT and 1010 both contained 3,5-DTBP.

Both Irgafos compounds degraded readily under the boiling water conditions, 168 produced 2,4-DTBP and other as yet unidentified materials and P-EPQ degraded to give 2,4-DTBP as the major product. Further investigations of the Irgafos P-EPQ standard and its residue remaining after boiling confirmed the presence of 2,6-DTBP, 3,5-DTBP, BHT and 2,4,6-TTBP. As noted earlier Irgafos 168 was also identified as being present in the standard of P-EPQ at a level of circa 12% w/w.

Analysis of the aqueous filtrate solutions of both Irgafos compounds confirmed the presence of 2,4-DTBP. In addition a significant amount of phenol and isomers of mono-tert-butylphenol were also found.

3.2.7.2 Identification of phosphite ester degradation products on reaction with peroxides

As previously mentioned in Section 3.1.3.1 phosphite esters are incorporated into the polymer matrix to inhibit the initiation step in autoxidation by decomposing hydroperoxides to alcohols. Ligner (193) used this ability to ascertain the amount of Sandostab P-EPQ in a polypropylene sample. By converting the extracted phosphite to the more stable phosphate using a dilute tert-butyl-hydroperoxide (TBHP) solution it was possible to quantify the amount present by HPLC with UV detection.

In this experiment a dilute solution of both hydrogen peroxide and TBHP solution were used to degrade standard solutions of Irgafos 168 and Irgafos P-EPQ. The resulting solutions were analysed and compared with previous data obtained from extraction and migration experiments on polyolefin samples.

Standard solutions of phosphites were prepared in acetonitrile (0.5mg cm^{-3}) and 2.0cm^3 of this solution was transferred to two 50cm^3 volumetric flasks. One flask being made up to volume with acetonitrile while the second had 1.0cm^3 of 30% w/v hydrogen peroxide added prior to making up. Both dilute sample and standard were then analysed by HPLC employing the chromatographic conditions cited in Table 3.8 for non polar analytes.

Analysis of the chromatograms produced showed that both phosphites had undergone degradation (Figure 3.9 & 3.10). On peroxidation of the dilute Irgafos 168 solution just one major component, and no residual phosphite could be detected. The retention time of this compound (13 minutes) being identical to one of the peaks found previously in migration and extraction experiments carried out on polyethylene films and polypropylene flasks (Figure 3.5c). Inferring that Irgafos 168 incorporated into the polyolefin has been oxidised to the phosphate by reaction with hydrogen peroxide (Eqs. 13).

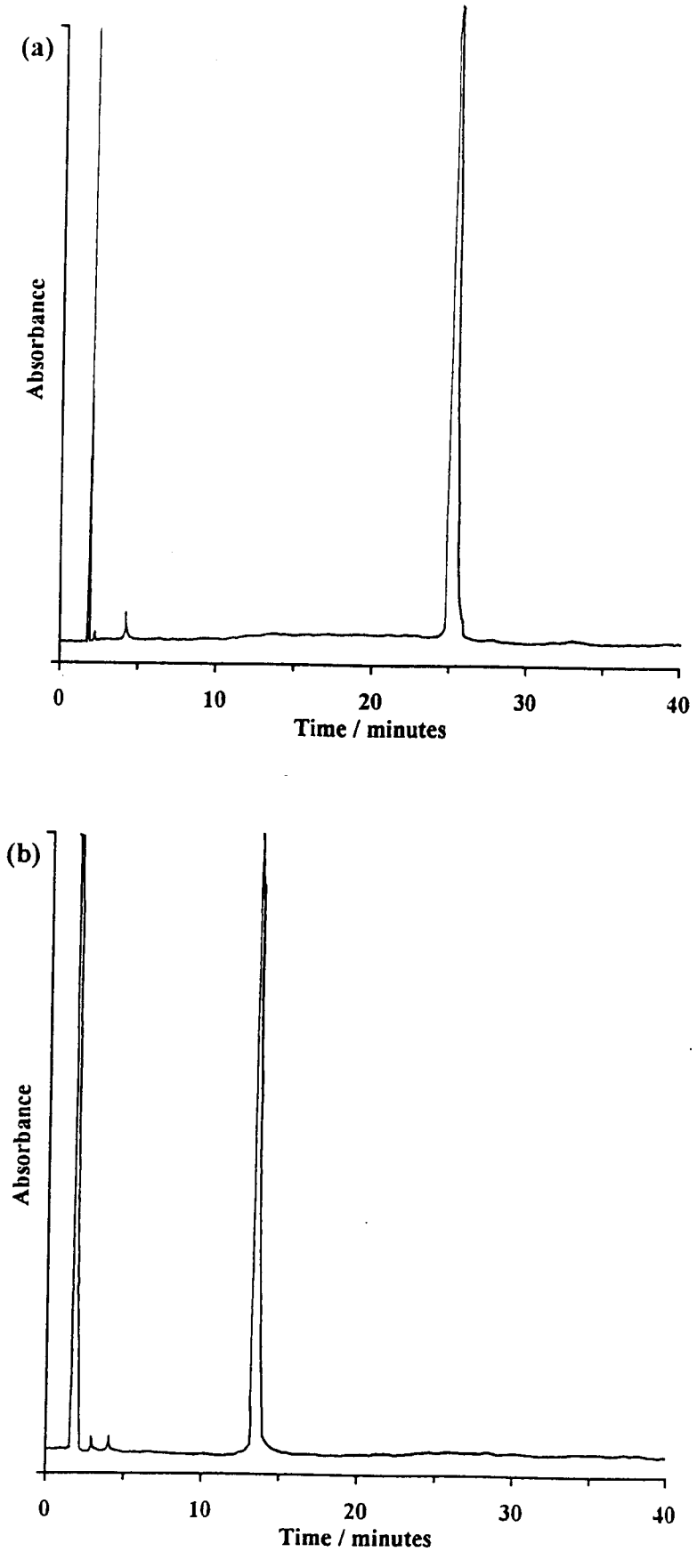


Figure 3.9 **HPLC Chromatograms obtained for :-**

a) Irgafos 168 **b) Peroxidised Irgafos 168**

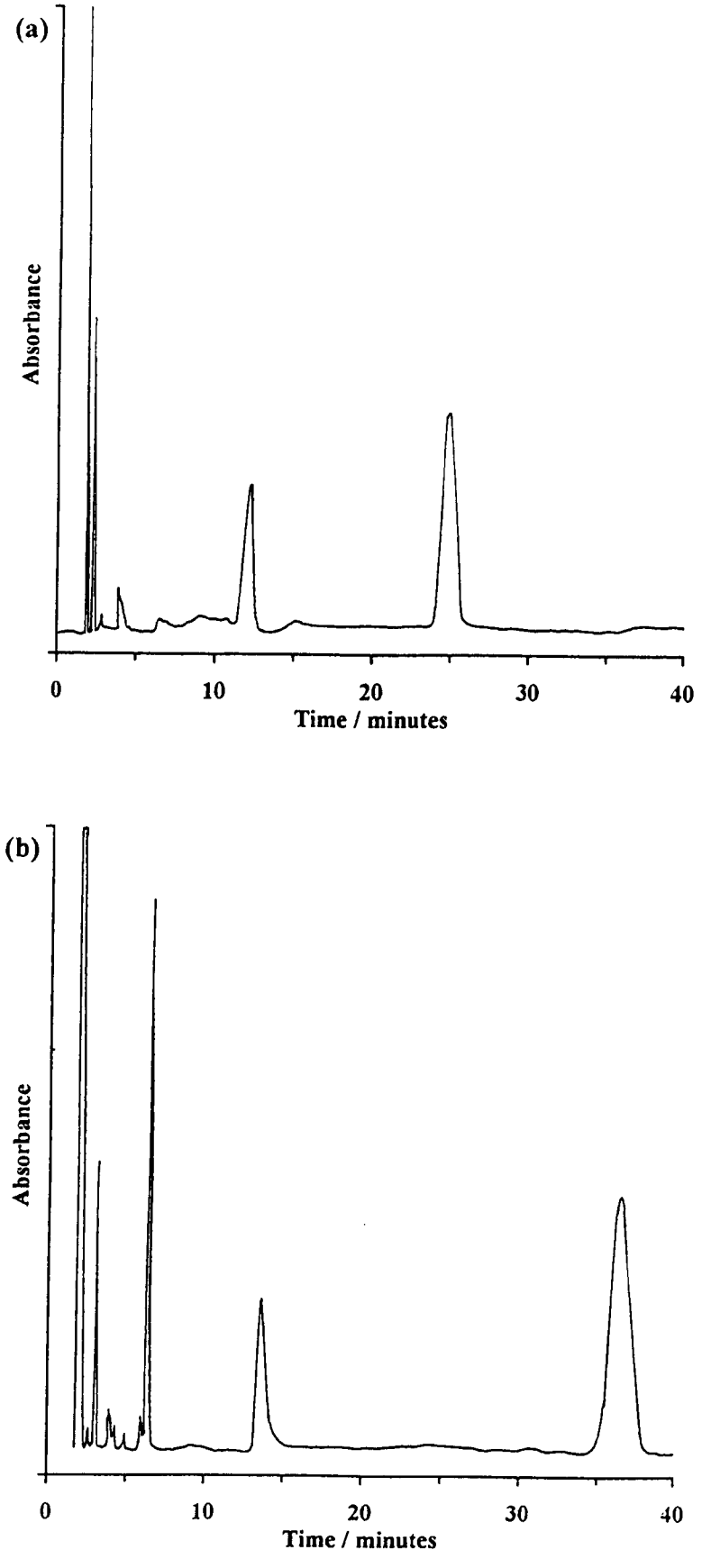
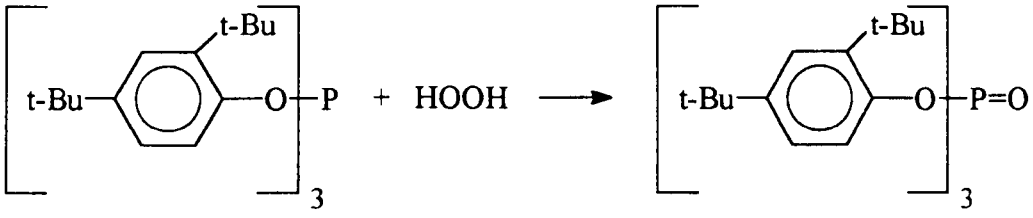


Figure 3.10 HPLC Chromatograms obtained for :-

a) Irgafos P-EPQ b) Peroxidised Irgafos P-EPQ



(Eqs. 13)

A similar fate was found to have occurred for the Irgafos 168 in P-EPQ. However, in addition a series of other components were found to be present. Postulations as to their identities were made by comparison with Ligners retention time data, but characterisation by HPLC could not be undertaken without suitable pure standards.

Hydrogen peroxide is such a strong oxidising agent that its reaction with the phosphite may lead to products which would not normally be expected under milder conditions, for example the use of tert-butyl-hydroperoxide (TBHP). So a 1% v/v solution of TBHP was prepared and reacted with both phosphite solutions as stated previously. Initial analysis of the chromatograms of the products of peroxidation of the phosphite solutions showed little difference to that of the corresponding standards. Only small amounts of the same products produced on reaction with hydrogen peroxide were observed. However, on standing for 5 days the chromatograms produced were virtually identical to those obtained previously when hydrogen peroxide was used.

In order to ascertain the identity of the compound produced on reaction of both hydrogen peroxide and TBHP with Irgafos 168 sufficient quantities had to be produced. To a standard solution of Irgafos 168 made up in a 2:1 (20 / 10cm^3) mixture of acetonitrile and dichloromethane was added 5cm^3 of 30% w/v hydrogen peroxide. On thorough mixing the solution was allowed to stand for one hour prior to the addition of excess dichloromethane, which facilitated separation from the aqueous hydrogen peroxide solution. The solvent layer after separation was then slowly evaporated down to dryness and the residue recrystallised using methanol. The crystals obtained were then air dried prior to further investigations.

Preliminary HPLC analysis of the degraded Irgafos 168 sample using the chromatographic conditions cited in Section 3.2.7 for non polar analytes, indicated the presence of just one component with no residual Irgafos 168 or other reaction by products.

Characterisation of the compound was then undertaken using direct probe mass spectrometry, infrared and multinuclear NMR techniques.

The direct probe MS analysis was carried out on the dried crystalline sample. The degraded Irgafos 168 sample was subjected to conventional electron impact mass spectrometry using a VG TRIO 3 instrument scanning over the mass range 30 to 700 daltons every second. The sample in the probe tip was rapidly heated to 300°C and several mass spectra were recorded during the sample elution. On volatilization of the crystalline sample the presence of ion m/z 663 was observed (Figure 3.11) which is the molecular ion that would be expected for oxidised Irgafos 168. Further comparison of mass spectra obtained from GC-MS analyses carried out on solvent extracts of polypropylene flasks and polyethylene films employing the same work up procedure cited in Section 3.2.3 indicated the presence of a compound with a similar mass spectrum (Figure 3.12).

Infrared (IR) analyses were carried out on both Irgafos 168 and the degraded Irgafos 168 sample and the resulting spectra compared. Small amounts of dried crystalline sample were compounded with potassium bromide to form a disc and the spectrum was recorded on a Perkin Elmer 683 Infrared spectrophotometer. Figures 3.13 & 3.14 show the IR spectra obtained. As can be seen on comparison of the IR spectra some differences between Irgafos 168 and the unknown compound are observed. One of the main differences appears in the Irgafos 168 where an intense absorption at 850cm^{-1} [P-O-C vibrations] is not present in the degraded Irgafos 168 sample. In comparison the degraded Irgafos 168 sample contains a strong absorption at 950cm^{-1} [P-O-C vibrations] in addition to an intense stretch at 1300cm^{-1}, which can be assigned to the P=O stretching frequency. When these differences in absorption are compared with the corresponding spectra obtained for the triphenyl-phosphite and phosphate (194) it can be seen that they have absorption bands for the P-O-C vibrations and P=O stretch at the same frequencies. Inferring that the compound produced on reaction of Irgafos 168 with dilute hydrogen peroxide has a similar structural conformation to triphenyl-phosphate, but is completely different to the starting material Irgafos 168.

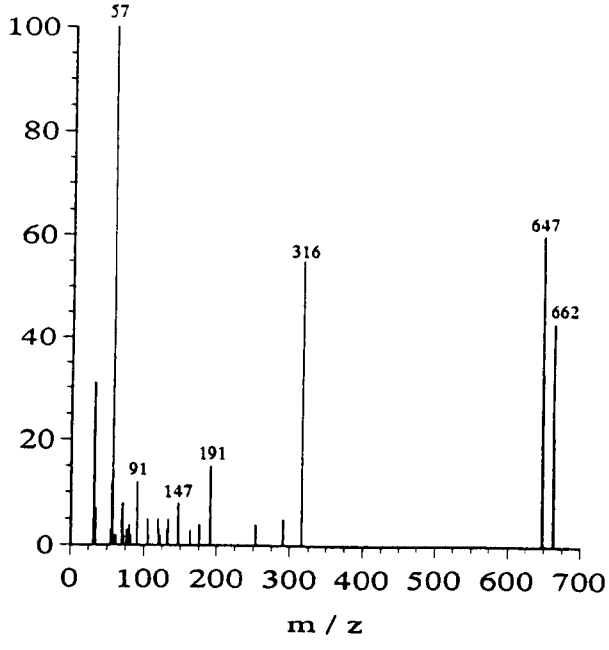


Figure 3.11 **Mass spectral data obtained from the direct probe analyses of the dried residue from the reaction of Irgafos 168 with H_2O_2**

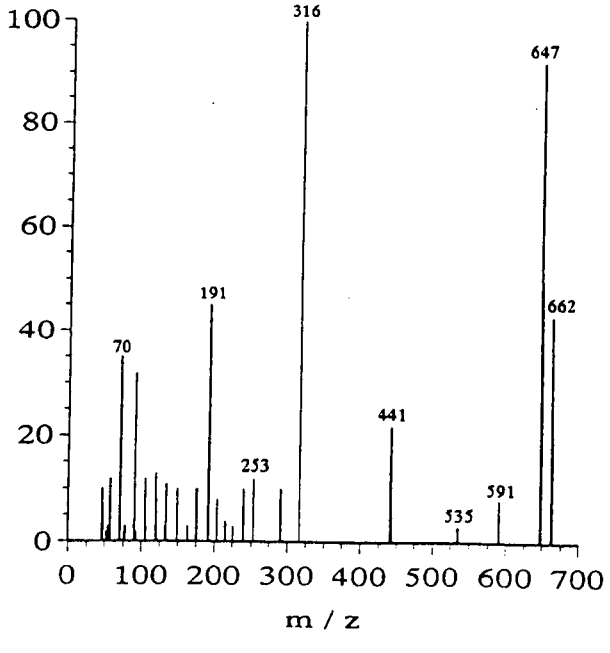


Figure 3.12 **Mass spectral data obtained from the GC-MS analysis of a dichloromethane extract of polypropylene flask**

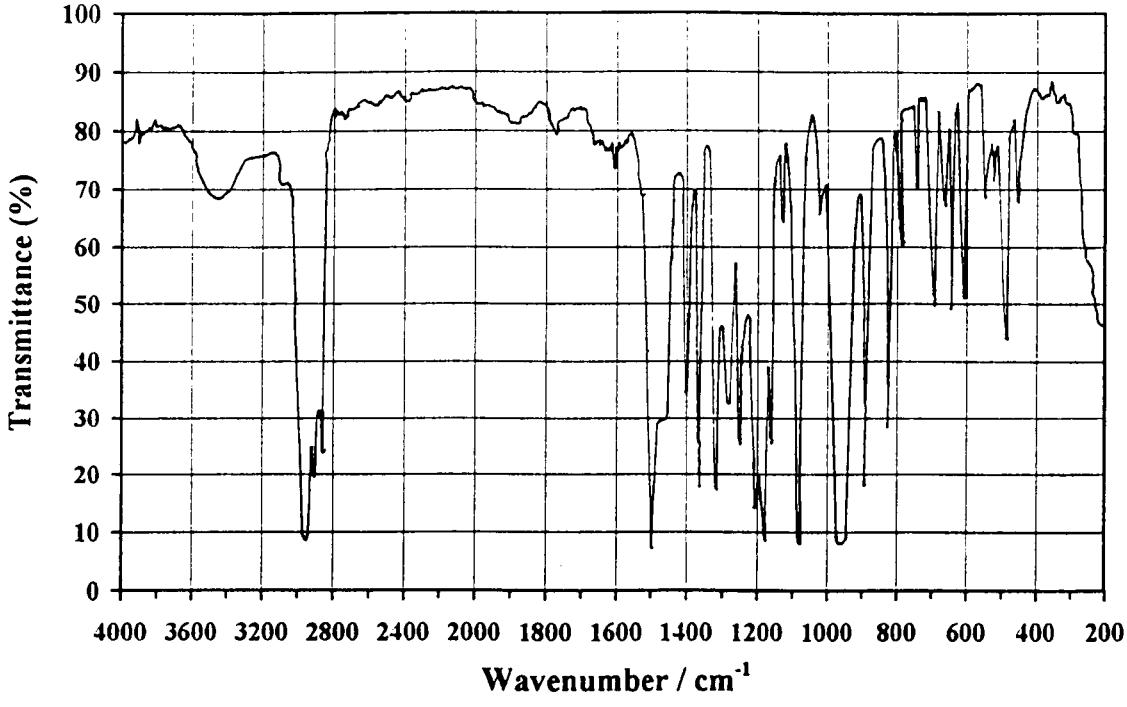


Figure 3.13 **IR Spectra of compound produced on reaction of Irgafos 168 with dilute hydrogen peroxide.**

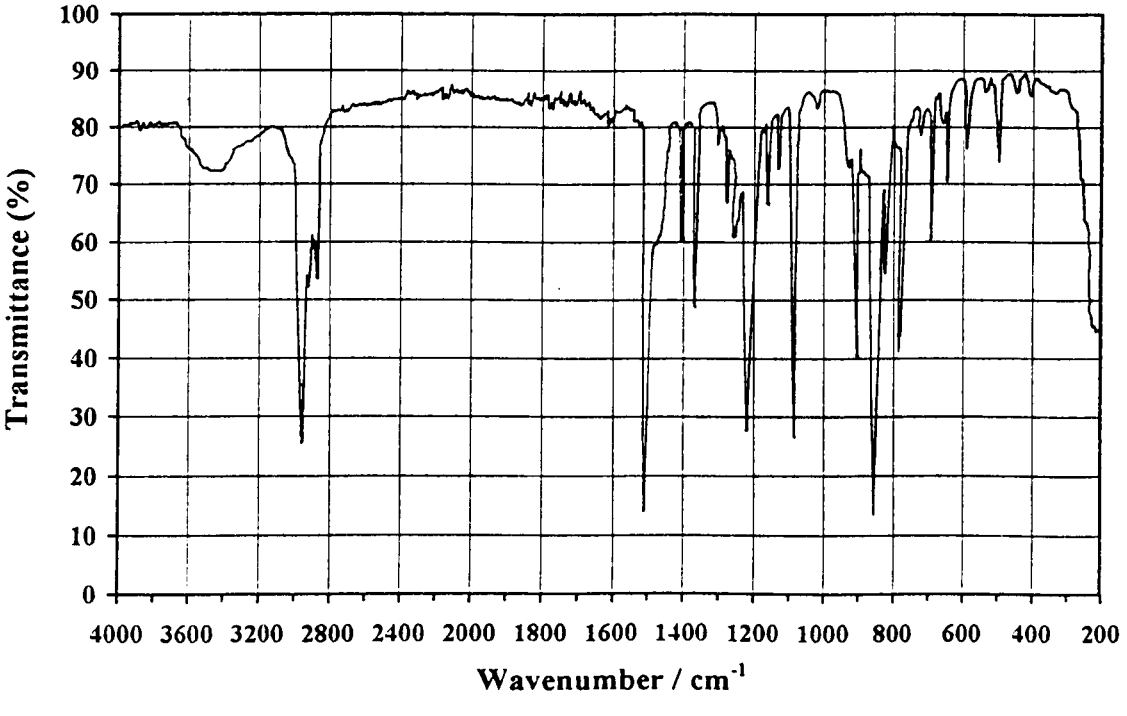


Figure 3.14 **IR spectra of Irgafos 168**

The NMR spectra obtained for both samples of Irgafos 168 and the compound produced on reaction of Irgafos 168 with hydrogen peroxide were recorded using a Bruker AC250 spectrometer. The spectroscopic conditions employed were as follows :-

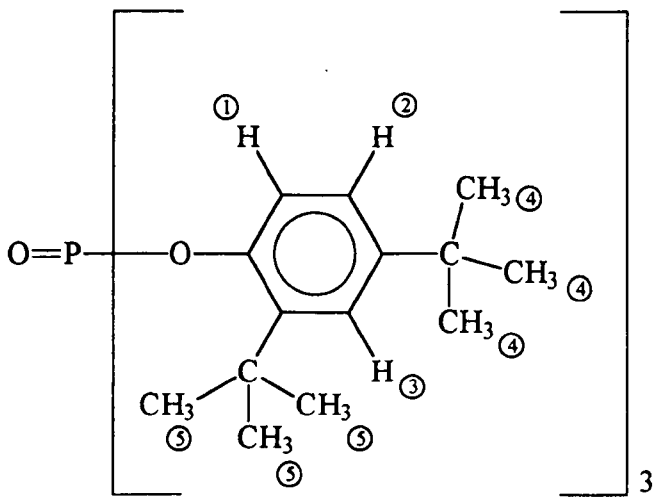
	$^{1}H_{(I)}$	$^{1}H_{(D)}$	$^{31}P_{(I)}$	$^{31}P_{(D)}$	$^{13}C_{(I)}$	$^{13}C_{(D)}$
Operating Frequency / MHz	250.13	250.13	101.26	101.26	62.90	62.90
Pulse Width / Hz	2.4	2.4	6.0	6.0	2.8	2.8
Sweep Width / Hz	4000	4000	21739	19231	16129	16129
Number of scans	16	16	123	313	2224	1053

Note : $_{(I)}$ = Irgafos 168

$_{(D)}$ = Degraded Irgafos 168

For ^{1}H and ^{13}C-NMR measurements both the standard Irgafos 168 and degraded Irgafos 168 sample were measured as 20% w/v solution in deuterated chloroform relative to tetramethylsilane (TMS). Whereas for ^{31}P-NMR, measurements were relative to 80% phosphoric acid. All measurements were undertaken at 303.3°K.

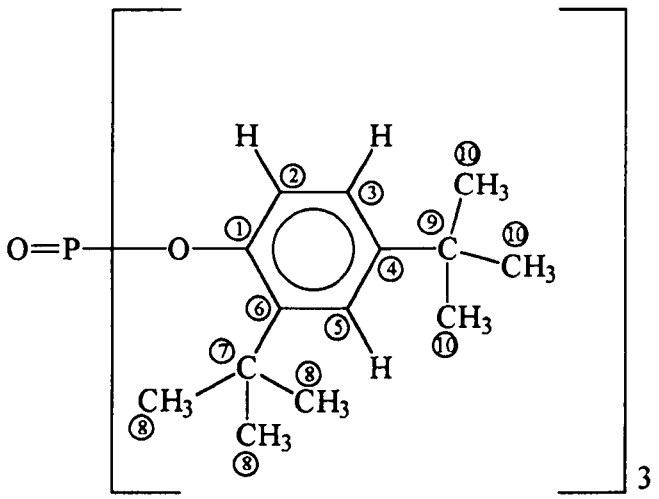
Figure 3.15 to 3.17 show the NMR spectra obtained and the detailed assignations of the spectra for ^{1}H-NMR and ^{13}C-NMR are shown in Tables 3.10 to 3.11 which match up with those predicted for oxidised Irgafos 168.



3

Peak Assignment	Type of Splitting	Integral	Chemical Shift / ppm	
			Irgafos 168	Degraded Irgafos 168
Ar $C(CH_3)_3$ **(4)**	s	9	1.3	1.3
Ar $C(CH_3)_3$ **(5)**	s	9	1.4	1.4
Ar H **(2)**	d	1	7.1	7.15
Ar H **(1)**	d	1	7.3	7.55
Ar H **(3)**	s	1	7.4	7.4

Table 3.10 **Assignation of the chemical shifts in ^1H - NMR spectra for Irgafos 168 and degraded Irgafos 168 sample**

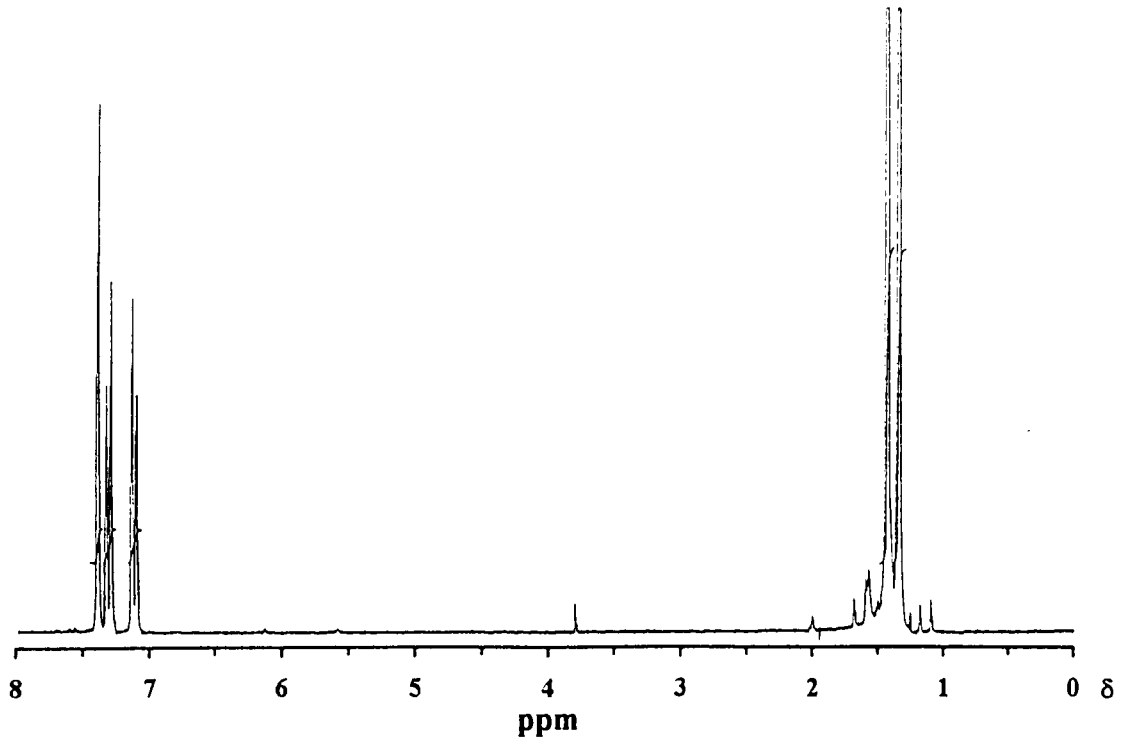


Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7 & C-9	C-8 & C-10
(I)	149.1	119.0	123.4	145.4	124.3	138.9	35-36	30-33
(D)	147.6	119.0	123.9	146.9	124.4	138.5	35-36	30-33

note : all chemical shifts are given in ppm relative to TMS as internal standard
(I) = Irgafos 168 where P=O not present
(D) = Degraded Irgafos 168 sample where P=O present

Table 3.11 **Assignation of the chemical shifts in ^{13}C - NMR spectra for Irgafos 168 and degraded Irgafos 168 sample**

(a)



(b)

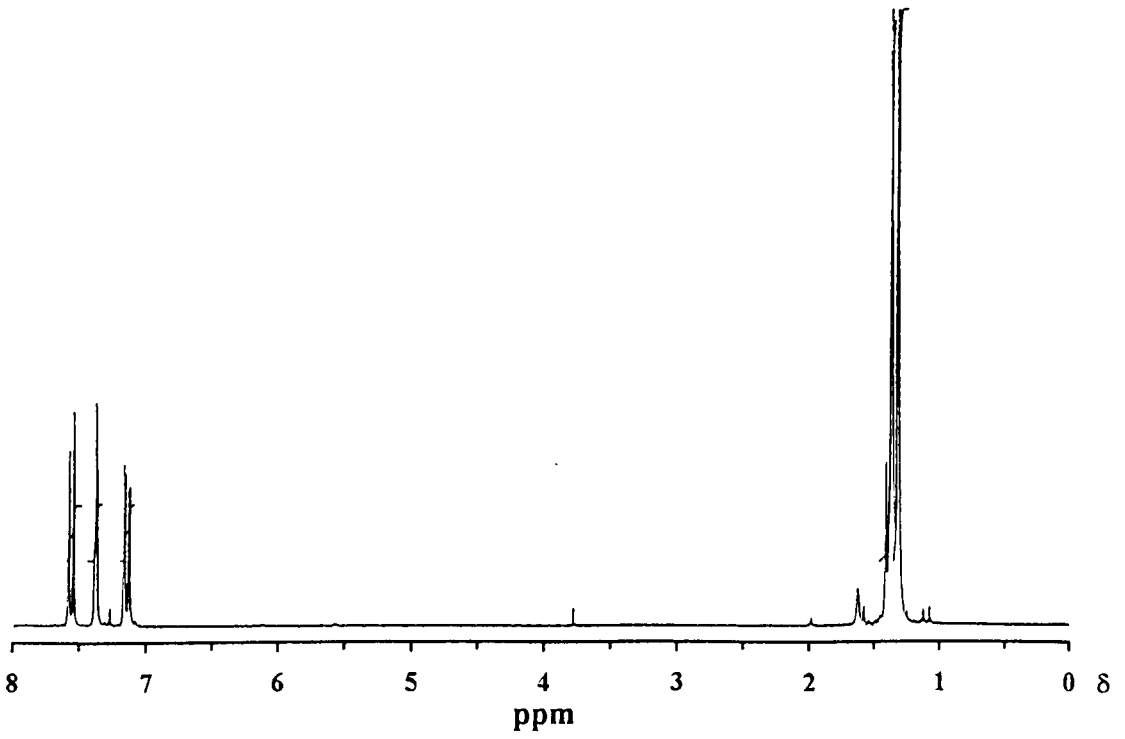
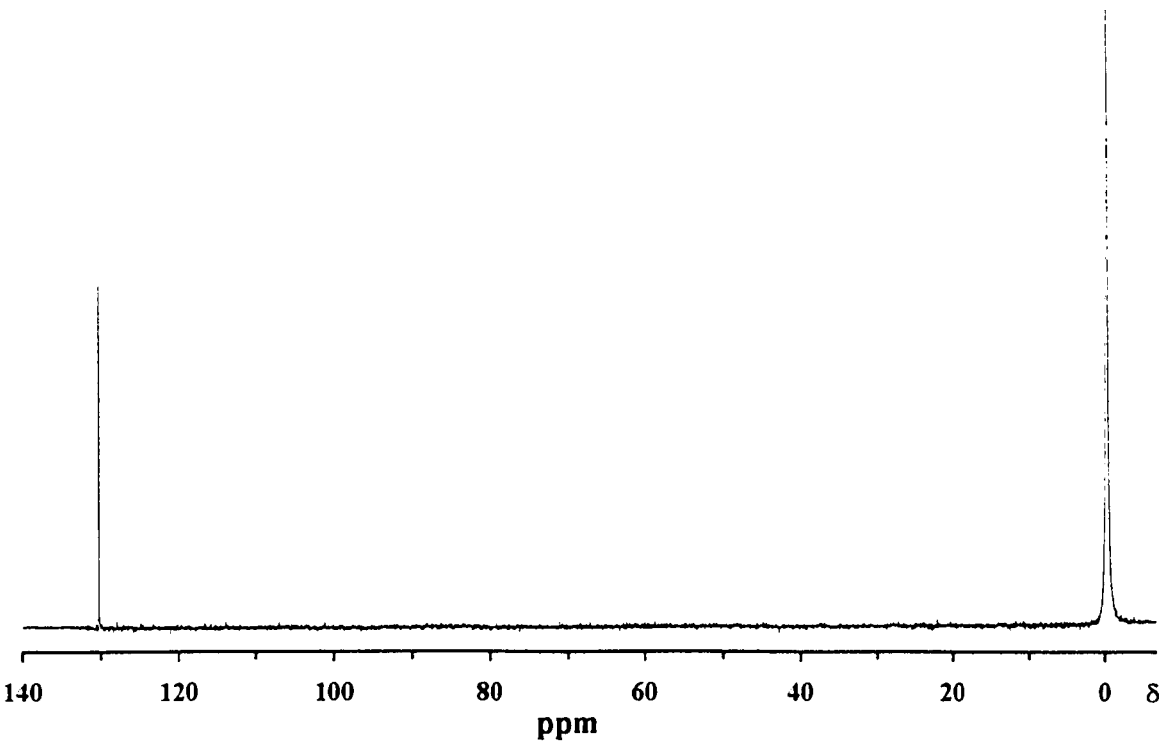


Figure 3.15 ^{1}**H - NMR spectra of :-** **a) Irgafos 168**

b) degraded Irgafos 168 sample

(a)



(b)

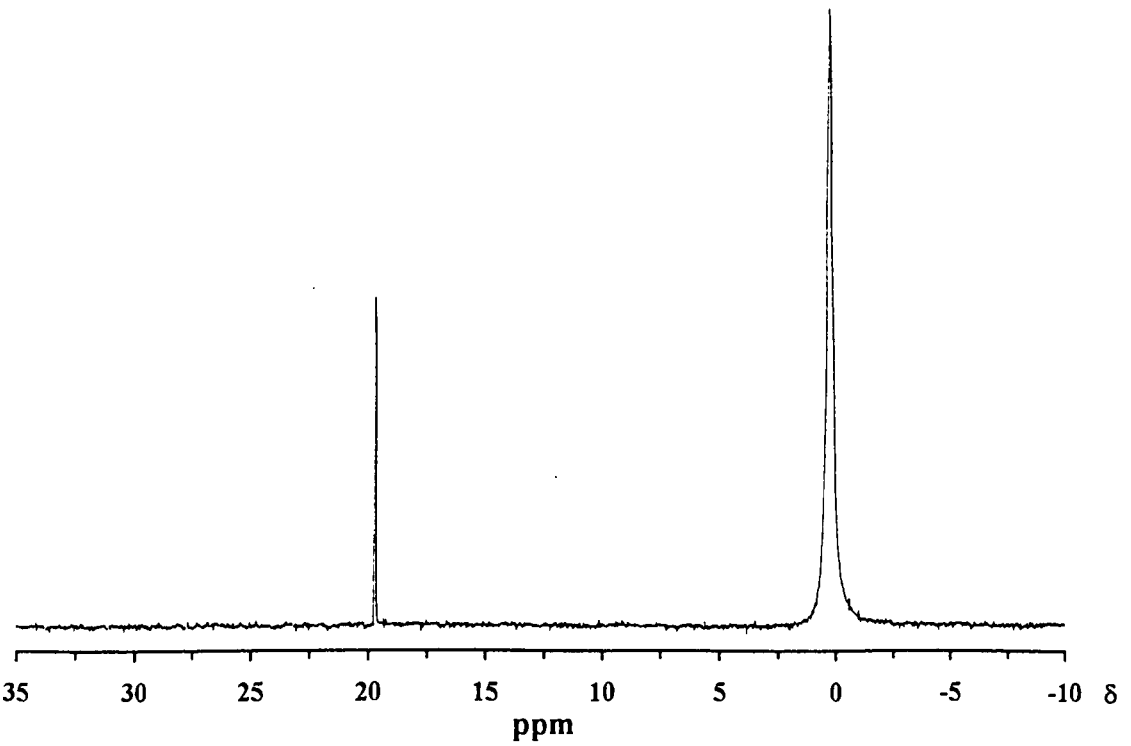
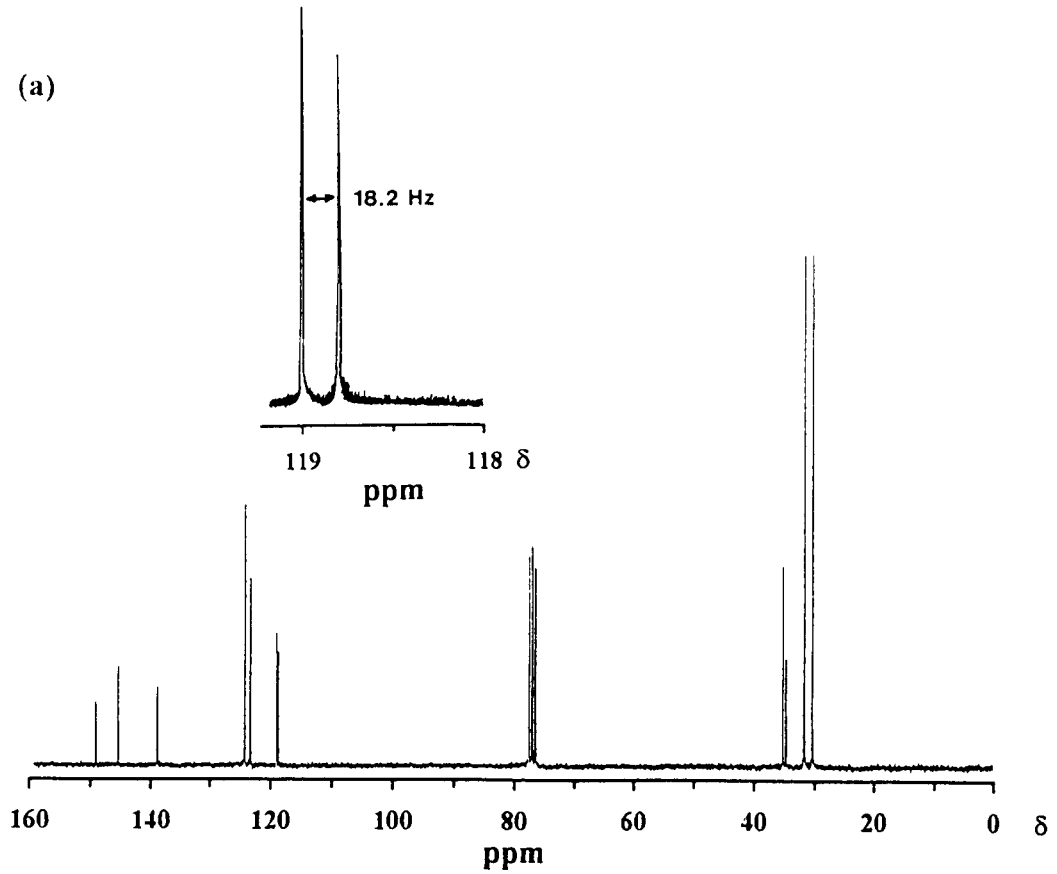


Figure 3.16 ^{31}P - NMR spectra of :- **a) Irgafos 168**

b) degraded Irgafos 168 sample



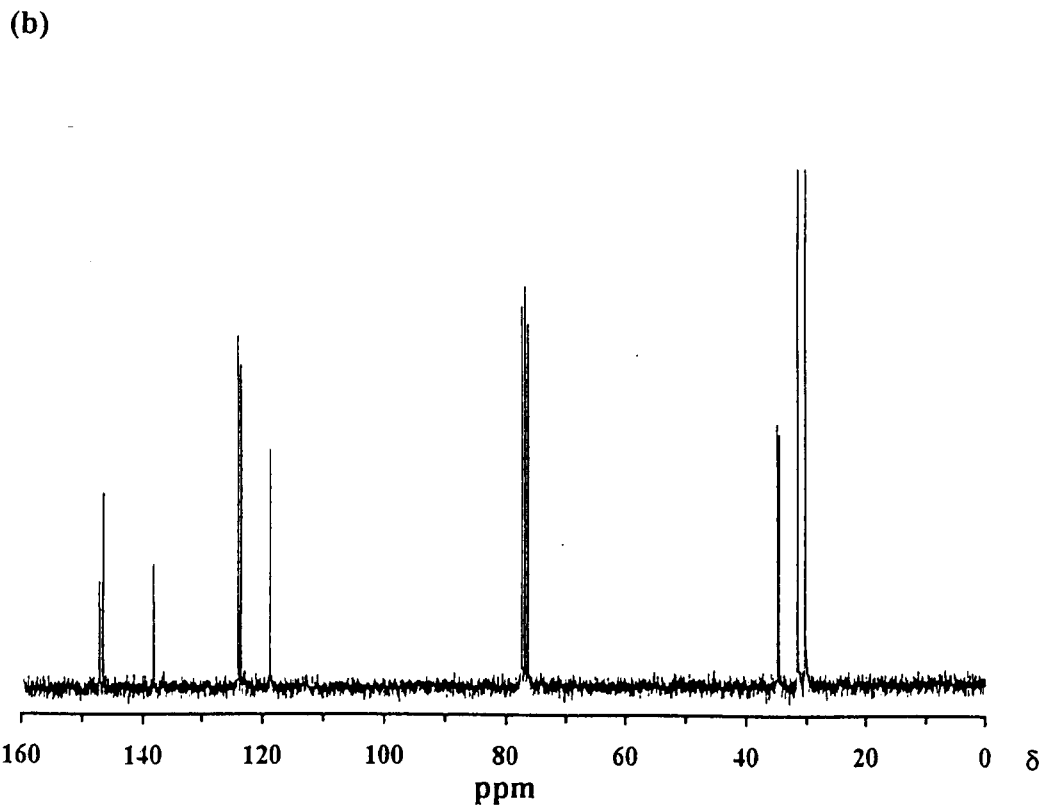


Figure 3.17 ^{13}C - NMR spectra of :- **a) Irgafos 168**

b) degraded Irgafos 168 sample

Comparison of chemical shift values obtained from the ^{31}P-NMR spectra for Irgafos 168 (phosphite) and the degraded Irgafos 168 sample (phosphate) showed close agreement to literature values (195). In addition no significant chemical shift associated with Irgafos 168 could be found in the degraded Irgafos 168 sample.

Some fine splitting is observed on the ^{13}C-NMR spectra for carbons ipso and ortho to the phosphite / phosphate groups, due to the ^{13}C-^{31}P coupling transmitted through oxygen atoms (196). The major anomaly is found in the ^{13}C-NMR spectra of Irgafos 168 at the chemical shift of 119ppm where a large ^{13}C - ^{31}P coupling (18.2 Hz) is observed for the C-2 carbon.

Employing the silicon graphics work-station the structure of both compounds were determined using its built in optimizing software (Figure 3.18 & 3.19). As can be seen the conformation of both structures are different, with the lone pair on the phosphorous in Irgafos 168 being in close proximity to C-2.

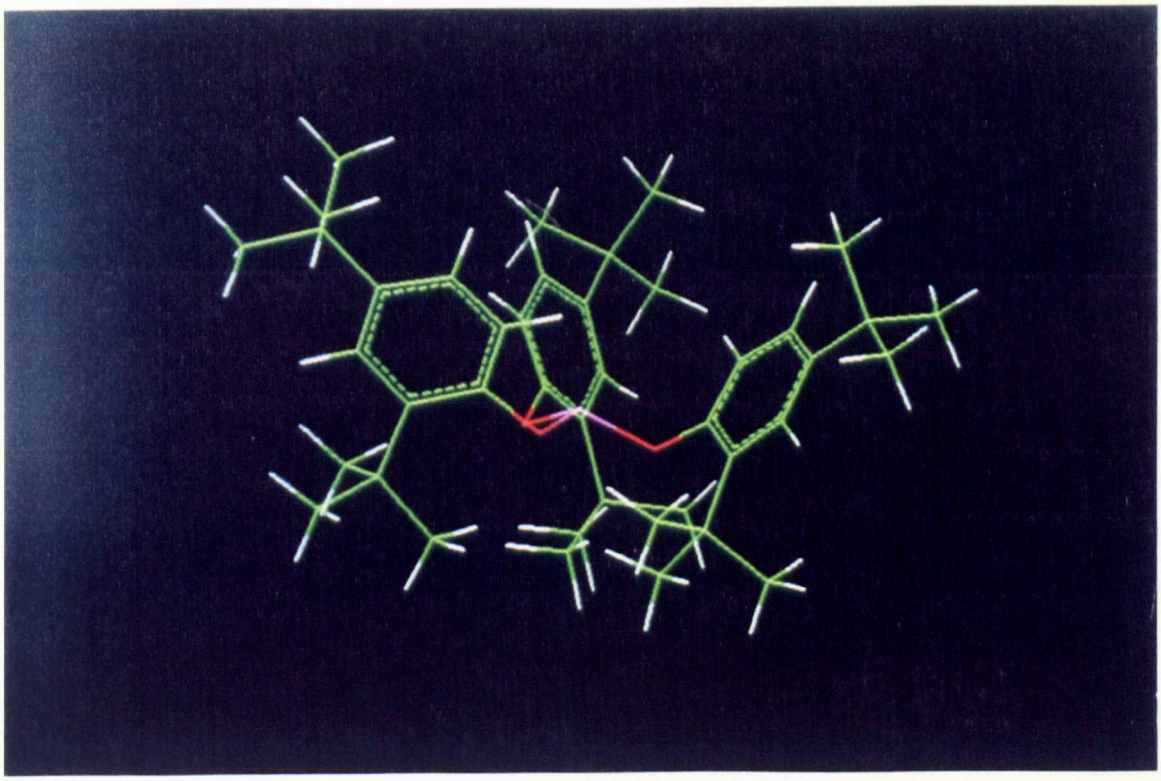


Figure 3.18 Structural conformation of Irgafos 168

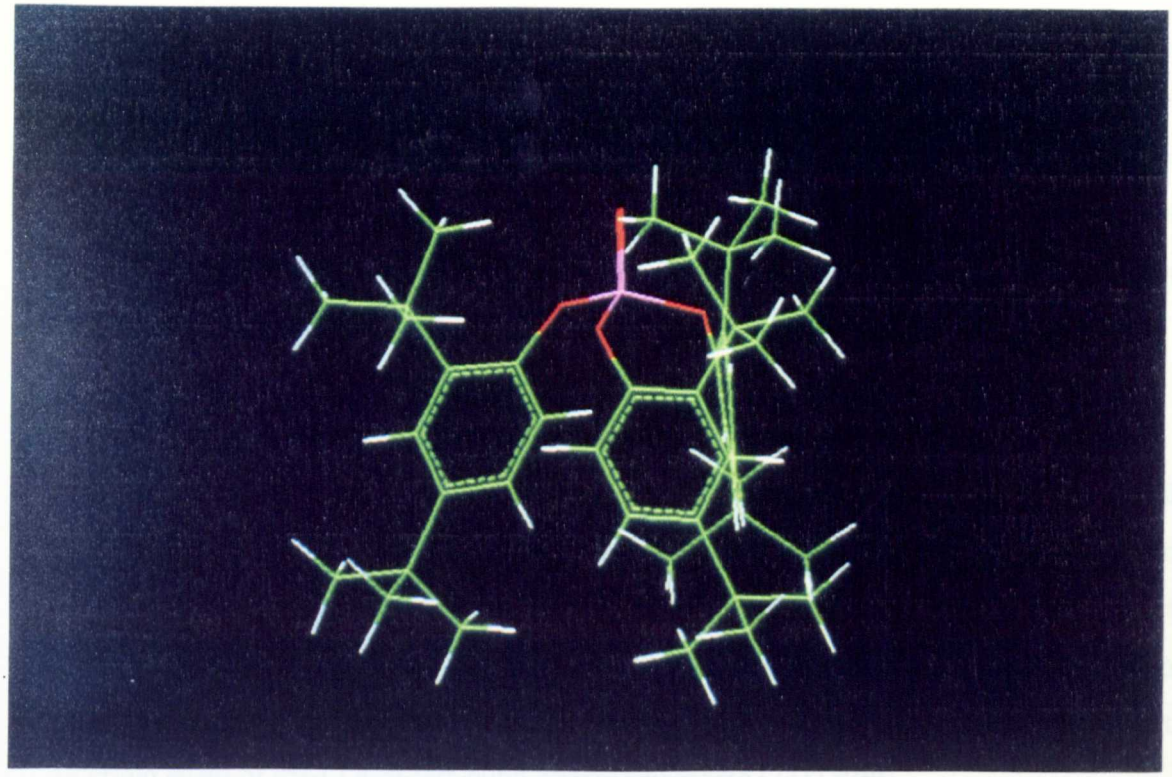


Figure 3.19 Structural conformation of oxidised Irgafos 168 [Tris (2,4-di-tert-butyl-phenyl)phosphate]

The unusually large coupling observed in the phosphite of 18.2 Hz is believed to be the result of interaction between the lone pair on the phosphorous and C-2. It has been reported (196-198) that the orientation of the lone pair in relation to the geminal carbon gives rise to a relatively large $^{2}J_{P,C}$ coupling constant when cis oriented with respect to the lone pair on the phosphorous. However, the effects of the lone pair on three bond coupling $^{3}J_{P,C}$ to C-2 and C-6 are not known due to a lack of comparable data. Haemers et al. (198) found that when the phosphorous lone pair in 1,3,2-dioxaphosphorinane stereoisomers was gauche - trans disposed to the vicinal carbon a much larger coupling constant was observed 13.5 Hz as opposed to 4.2 Hz for trans - trans. In phosphites the position of the lone pair in relation to the vicinal carbon (3 bond coupling) is found to be more important than the Karplus effect. In the phosphate this coupling is not detected as a result of conformational and oxidation state changes.

From the results and data observed it can be stated that the main product of the reaction of Irgafos 168 with either 30% w/v hydrogen peroxide or dilute tert-butyl-hydroperoxide is oxidised Irgafos 168 [tris-(2,4-di-tert-butyl-phenyl)phosphate]. From comparison of retention time data employing HPLC this compound has been identified as being present in previous migration and extraction experiments carried out on polyethylene films and polypropylene flasks. Further investigation using GC-MS confirmed the presence of this species.

3.2.7.3 Quantification of antioxidant degradation products in polyolefins

The film and flask / kettle body samples were exhaustively extracted with acetonitrile (Section 3.2.3), and the resultant solutions were assessed using the methods developed for monitoring the degradation products. Quantification of the antioxidant degradation products in the polyolefin samples were determined using HPLC and the following equations based on external standard calibration methods. The oxidised Irgafos 168 sample prepared was used to ascertain levels of tris-(2,4-di-tert-butyl-phenyl)phosphate (TDTBPP).

$$\text{Concentration of antioxidant degradation product } (\mu g\ dm^{-2}) = \frac{A_{SPL} \times C_{STD} \times V_S}{A_{STD} \times A_{PO}}$$

$$\text{Concentration of antioxidant degradation product } (\mu g\ g^{-1}) = \frac{A_{SPL} \times C_{STD} \times V_S}{A_{STD} \times M_{PO}}$$

Where :-

A_{SPL} = Peak area of antioxidant degradation product

A_{STD} = Peak area of external standard

C_{STD} = Concentration ($\mu g\ cm^{-3}$) of external standard

A_{PO} = Area (dm^2) of polyolefin in contact with solvent / food simulant

M_{PO} = Mass (g) of polyolefin sample

V_S = Final volume (cm^3) of extracting solvent / food simulant

Polyolefin Sample	Amount / μg dm^{-2}			
	3,5-DTBP	2,4-DTBP	2,4,6-TTBP	TDTBPP
NEW FILMS				
15μm LLDPE	2.8	5.6	3.9	11.0
50μm LLDPE	3.5	11.1	6.0	34.0
NEW FILM				
15μm HDPE	2.2	3.1	3.7	15.0
OLD FILMS				
15μm LLDPE	3.2	7.3	14.0	67.0
50μm LLDPE	76.0	44.0	65.0	110.0
OLD FILMS				
15μm HDPE	8.3	16.1	14.0	11.0
50μm HDPE	69.1	83.2	65.0	24.0
POLYPROPYLENE	10.8	4.3	5.2	170.0

Note : all data subject to a ± 10% variation

Table 3.12 Antioxidant degradation product levels in polyolefin expressed as mass / unit surface area in contact with solvent

From Table 3.12 it can be seen that the largest quantity of antioxidant degradation products are found in the old polyethylene films. These films are four years old so the antioxidants are being converted to these products as a direct result of them preventing the polymer from undergoing autoxidation by ageing. Much smaller quantities were found in general to be extracted from the new polyolefin samples. The one exception being the significant amount of TDTBPP extracted from the polypropylene flask / kettle body samples. However, the polypropylene mass per unit area for these samples is large and when this is taken into consideration the amount extracted in μg g^{-1} of polymer is similar to that obtained for the polyethylene films.

3.2.7.4 Quantification of antioxidant degradation products migrating from polyolefins

Antioxidant degradation products migrating from new polyethylene films and polypropylene flask / kettle bodies into aqueous and oil simulants were determined employing the methodology developed (Section 3.2.7). Migration studies were carried out as detailed previously in Section 3.2.5 with quantification by external standard calibration methods.

The results obtained are compiled in Table 3.13. The data is in the most part analogous to that for the parent antioxidants with smaller levels migrating from the polymer into water than silicone oil. Similar levels of antioxidant degradation product, initially present in the polyethylene films after processing, were found to migrate into the silicone oil after one hour. The same was found to occur for the TDTBPP even though the polypropylene was substantially thicker. This can be rationalised on the basis that Irgafos 168 on the surface of the polymer has undergone degradation during the production process (injection moulding).

Polyolefin Sample	Amount / μg dm^{-2}			
	3,5-DTBP	2,4-DTBP	2,4,6-TTBP	TDTBPP
WATER				
New films				
15μm LLDPE	0.2	< 0.1	ND	ND
50μm LLDPE	0.1	< 0.1	ND	ND
15μm HDPE	0.1	< 0.1	ND	ND
Polypropylene	1.7	0.2	ND	ND
SILICONE OIL				
New films				
15μm LLDPE	3.2	6.4	5.7	8.1
50μm LLDPE	4.0	12.2	3.8	16.3
15μm HDPE	3.0	3.0	5.8	14.1
Polypropylene	8.9	3.6	6.0	200.0

Note : all data subject to a ± 10% variation
ND = Not Detected

Table 3.13 Migration of antioxidant degradation products from selected polyolefin samples into different food simulants

3.2.8 Quantification of migrants produced by steam distillation

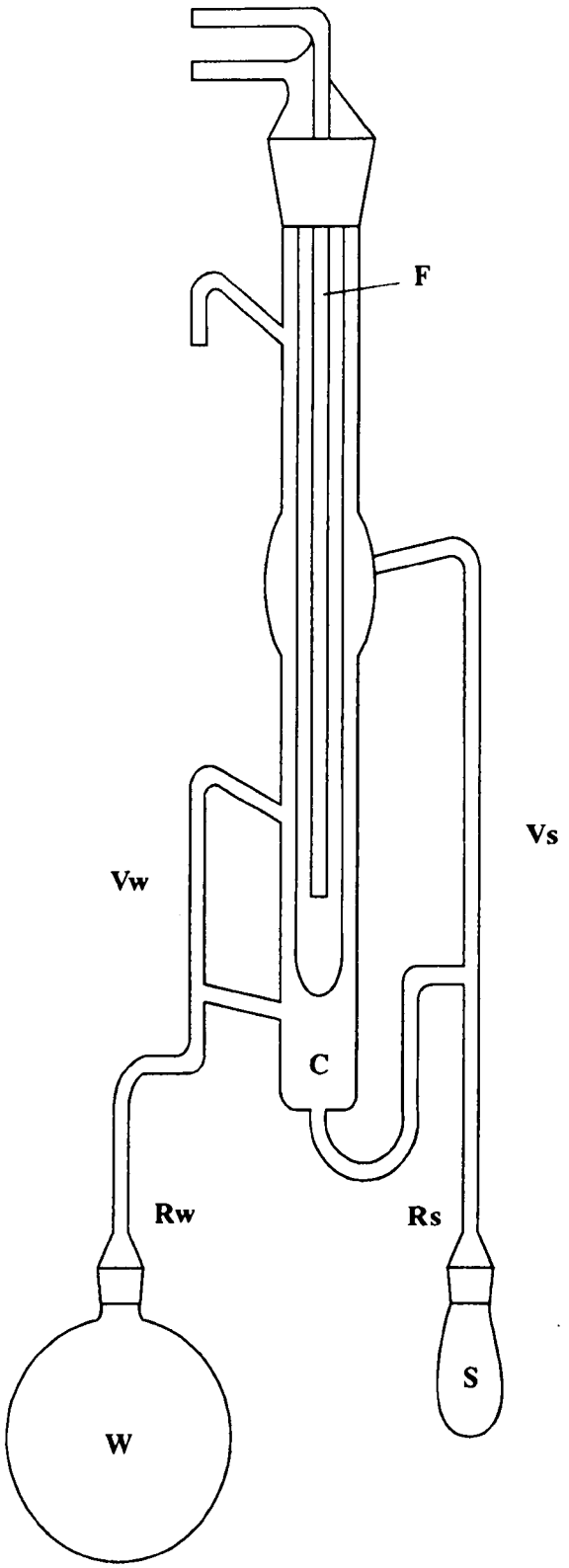
Internal steam distillation can occur particularly in a kettle body and lid such that extracted material could be returned to the bulk of the water in the utensil. Work published by Rebeyrolle and Etiévant (199) cited the extraction of aldehydes, ketones, carboxylic acids and antioxidant fragments from polypropylene granules by steam distillation. In the investigation reported here small granules (2 × 2mm) of the polypropylene were treated in a micro steam distillation apparatus (Figure 3.20) and concurrently the resultant distillate was extracted with dichloromethane. The aqueous simulant, 50cm^3 was placed in flask (W) with circa 7g of polymer granules and 10cm^3 of dichloromethane was added to the solvent flask (S). Both flasks were heated and the steam and dichloromethane mixed, condensed and were run off separately as shown in Figure 3.20. After a four hour exposure period the dichloromethane extract was evaporated to dryness in an inert atmosphere, made up to 5cm^3 in acetonitrile and analysed using the methodology outlined previously. Again quantification was undertaken using the equation in Section 3.2.7.3 based on external standard calibration methods.

Within the limits of the chosen analytical techniques the following compounds were found to be present in the distillate.

Compound	Amount / μg dm^{-2}	Amount / μg g^{-1}
3,5-DTBP	7.0 ± 0.9	3.5 ± 0.5
2,4-DTBP	6.8 ± 0.5	3.4 ± 0.3
2,4,6-TTBP	3.2 ± 0.5	1.6 ± 0.3

Table 3.14 Antioxidant degradation products in distillate

From the data obtained it can be seen that the migration values for these antioxidant degradation products in the distillate are larger than those determined for an aqueous food simulant. This is a result of the antioxidant degradation products being transferred from the water to the dichloromethane. Therefore a concentration effect is experienced as the material present in the evaporating water is removed by the dichloromethane allowing more material to migrate into the water.



Abbreviations:

W : Flask for water
S : Flask for solvent
F : Condensor
C : Separation chamber

Vw : Vapour tube for water
Vs : Vapour tube for solvent
Rw : Return tube for water
Rs : Return tube for solvent

Figure 3.20 Micro steam distillation apparatus

3.3 SUMMARY

This work has confirmed the presence of antioxidants and their degradation products migrating into aqueous and oil simulants from polyolefins. In general relatively low levels of migration, particularly into aqueous simulants have been measured. As anticipated significantly more were found to migrate when an oil simulant is used due to its ability to penetrate the polymer matrix and modify the local environment.

The thickness and morphology of the polyolefin sample played a significant part in the quantity of antioxidants migrating. At comparable temperatures and exposure times to the same food simulants, the percentage of available antioxidants migrating from the different classes of polyolefin analysed decreased in the order LLDPE > HDPE >PP. As expected the thicker polypropylene samples used in flasks and kettles produced a greater mass of migrants and required a longer extraction time for the removal of residual antioxidants. HPLC and UV analysis indicated that initially the majority of the migrants in food simulants were antioxidant degradation products and other production aids which were left on the surface of the polypropylene after production. On repeated extraction with an aqueous food simulant these were removed and the initial levels of antioxidant Irganox 1010 began to increase. Eventually after 5 × 1 hour exposures to boiling water the levels of migrants plateaux out as the amount of antioxidant and their degradation products blooming on the surface of the polypropylene reached an equilibrium.

Analysis of the commercial antioxidant Irgafos P-EPQ which is used in the manufacture of polyolefins indicated the presence of 12% w/w Irgafos 168, which is found to migrate into food simulants. Both of the Irgafos antioxidants were also found to degrade on boiling for 4 hours in water to give 2,4-DTBP as the major product. In addition in the process of decomposing hydroperoxides present in the polyolefin they are readily converted to their corresponding phosphates. GC-MS and HPLC data confirmed the presence of the phosphate of Irgafos 168 [tris-(2,4-di-tert-butyl-phenyl)phosphate] in the initial polyolefin samples as well as the food simulant extracts of the polyolefins. Other antioxidant degradation products which were found to migrate included 2,4-DTBP, 3,5-DTBP and 2,4,6-TTBP. Significant quantities of these antioxidant degradation products were also found in steam extracts of polypropylene samples. For kettles where this material is employed these compounds will evaporate off with the steam on boiling. However, on addition of boiling water to a flask which has a polypropylene insert these compounds will be retained due to it being a sealed container.

CHAPTER 4 : POLYAMIDES

4.1 INTRODUCTION

When Carothers (100) discovered polyamides over sixty years ago, he could not have imagined the range of current diverse applications of the silk substitute he had created. From basic fibre origins in 1938, the polyamide family has grown into one of immense proportions and versatility.

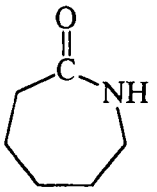
Nylon is a generic term for any long chain synthetic polymeric amide, in which recurring amide groups are integral to the main polymer chain. There is a wide choice of starting materials from which polyamides can be synthesized. The two primary methods for manufacture are, condensation of a diamine and a dibasic acid or their equivalents, and polymerization of monomeric substances. In practice comparatively few nylons are available commercially. Nylon 6 and nylon 6,6 constitute 90% (101) of world-wide domestic sales volume (351,000 and 367,000 metric tons respectively in 1988), largely because they offer the most favourable combination of price, properties and processability.

The toughness of polyamides has made them the material of choice in Europe for a variety of food packaging applications for almost forty years. They offer a combination of properties including high tensile strength (especially at elevated temperatures up to 140°C), flexibility at low temperatures, good abrasion resistance, and very good gas barrier properties. Chemically, polyamides are resistant to weak acids, strong alkalis, and are particularly resistant to organic solvents, oils and greases.

In Europe nylon 6 film, and to a lesser extent nylon 6,6 are the most commonly used polyamides in the flexible packaging market. However both of these films are not widely used on their own as packaging films because of their sensitivity to water and consequently high moisture vapour permeability. As a result most of the films are used in conjunction with other plastics, resulting in composites utilizing the characteristics of each material in the construction. Polyamides are commonly combined (laminated / coextruded) with polyethylenes for food packaging applications where the oxygen barrier capabilities of polyamides and the moisture barrier characteristics of polyethylene are required.

4.1.1 Nylon 6

Nylon 6 is produced by the hydrolytic bulk polymerization of caprolactam monomer (202-204) using either batch or continuous processes. The caprolactam ring is hydrolysed under high pressure steam conditions to open the lactam ring and form the more reactive aminocaproic acid.



+ H_2O $\xrightleftharpoons{\text{Acid Catalysed}}$ $NH_2\,(CH_2)_5\,COOH$

Caprolactam ring **Aminocaproic Acid**

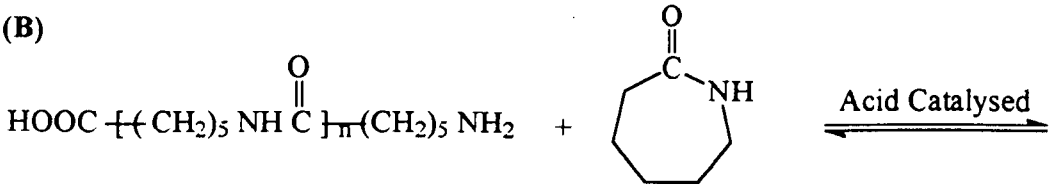
Polymerization proceeds by polycondensation **(A)** of the aminocaproic acid and by the addition of caprolactam to the amine end groups with subsequent opening of the lactam ring **(B)**.

(A)

$$_{(n+1)}\ HOOC\,(CH_2)_5\,NH_2 \xrightleftharpoons{\text{Acid Catalysed}} HOOC\text{-}\{\{(CH_2)_5\,NH\,\overset{O}{\overset{\|}{C}}\}_n(CH_2)_5\,NH_2$$

$$+\ n\,H_2O$$

(B)



$$HOOC\text{-}\{\{(CH_2)_5\,NH\,\overset{O}{\overset{\|}{C}}\}_{n+1}(CH_2)_5\,NH_2$$

Nylon 6

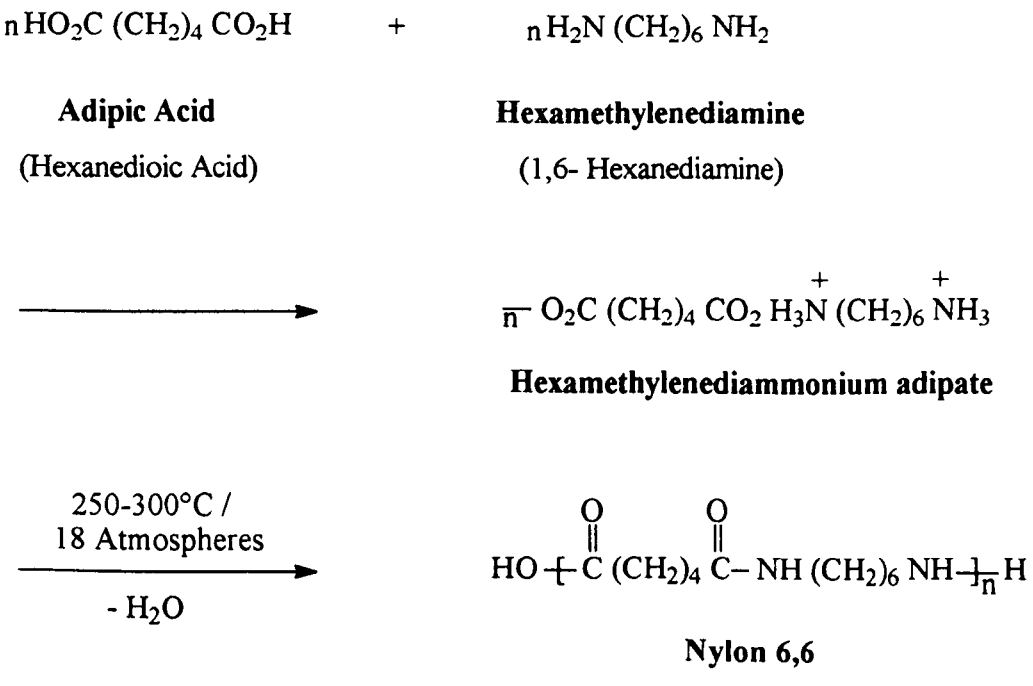
The reaction proceeds to about 90% conversion leaving a residue of mixed monomer and low molecular weight oligomers. These residues are removed either by leaching or vacuum treatment of the polymer melt (205).

Resin pellets used for film production are slurried in water and pumped into leaching towers where countercurrent extraction using water at 95°C takes place. The monomer and oligomers are reduced in level to around 2% w/w and the pellets are then dried to 0.2% residual water before further processing.

4.1.2 Nylon 6,6

Nylon 6,6 is manufactured by the condensation reaction between equimolar quantities of hexamethylenediamine and adipic acid (206). The resulting solution of hexamethylenediammonium adipate which precipitates on mixing the monomers is then adjusted to the correct pH and heated under pressure to about 250°C. Under these conditions condensation begins and amide linkages form accompanied by the generation of water which is continuously removed.

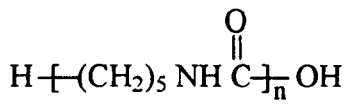
The resin pellets produced contain approximately 1% residual water at this stage, but washing and drying are not necessary if proper stoichiometric balances are maintained throughout the polymerization cycle.



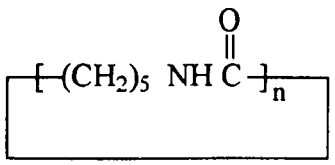
The nylon 6,6 and nylon 6 resin pellets are then converted into films by either the flat casting or blown film process, resulting in cast and oriented films respectively (207). By orienting the nylon film biaxially the transparency, water vapour and gas permeability properties are improved.

4.1.3 Polyamide oligomers

In polyamides hydrogen bonding is a major contributor to the intermolecular cohesion, and residual water in the polymer reduces the intermolecular forces and essentially acts as a plasticizer (208). Reported analyses of residual oligomers in nylon 6 films have indicated extracted levels of around 1.4% w/w (209). The nature of the extracted oligomers is uncertain, there is evidence for both cyclic (210-211) and linear species (212). The production of a cyclic species would appear to preclude that material from further reaction and thus prevent it being bonded into the polymer matrix since the free amine end group is not available for further polymerization. Residual cyclic oligomers would therefore seem to be more readily available than the linear version.



Linear Oligomers Nylon 6



Cyclic Oligomers Nylon 6

4.1.4 Toxicological and legislative aspects

A number of toxicity studies have been published in support of the safety of nylon 6 / 6,6 copolymers for non food contact use in laminates intended for cooking and storing foods (213-214). The results of these studies give no indication of any carcinogenic potential in caprolactam, but there are signs that it is slightly toxic. Caprolactam has been shown to be a mild circulatory depressant, a potential respiratory stimulant and to cause mild reversible depression. However, because of its rapid elimination from the body it is considered to have a low order of toxicity in humans (215).

Caprolactam has been assessed by the Scientific Committee for Food (SCF), and they have established a tolerable daily intake (TDI) of 0.25mg kg^{-1} or 15mg a day for a 60 kg person (25). The list of authorised monomers and other starting materials (Section A) laid down in directive 90/128/EEC (20) also states a specific migration limit (SML) for caprolactam into food or food simulants of 15mg kg^{-1}. However no such SML exists for any of the oligomers of caprolactam. Toxicity tests carried out on rats fed with a diet of nylon 6 cyclic oligomers did not reveal any distinct toxic effects (216). A no effect level was established at 2-4% in the diet of rats over a period of three months, which equates to 2000mg kg^{-1} body weight per day.

The starting materials, adipic acid and hexamethylenediamine used in the manufacture of nylon 6,6 have also been authorised for use in articles intended to come into contact with food (20). For adipic acid the SCF have established an ADI of 5mg kg^{-1} body weight, and a TDI of 0.04mg kg^{-1} for hexamethylenediamine (25). Directive 90/128/EEC also states a SML in food or food simulant for hexamethylenediamine of 2.4mg kg^{-1}.

4.2 EXPERIMENTAL

In the application under investigation nylon 6 / 6,6 will only be in contact with aqueous media, on the outside of a boil-in-bag, and therefore all work was restricted to migration into 18MΩ millipore water.

In order to investigate these migrants from nylon 6 and 6,6 into boiling water a series of experiments were undertaken on five commercially available films. In each case a total immersion method was employed, with the polymer chopped into 1cm squares, to facilitate compound migration and identification.

4.2.1 Materials

Sample Films

The five nylon films used in these investigations were all of commercial quality. Their dimensions were carefully checked and the mass of a known area of film was determined for subsequent migration calculations (see Appendix 1).

Sample		Type of nylon film
15 μm	Nylon 6	Oriented
20 μm	Nylon 6,6	Cast
25.4μm	Nylon 6	Cast
50 μm	Nylon 6	Cast
80 μm	Nylon 6	Cast

Reagents

The following reagents were used:

Millipore water - (resistivity 18MΩ cm -milli-RO15 water system)

HPLC grade acetonitrile and HPLC grade methanol
(Rathburn, Walkerburn, U.K.)

ε-Caprolactam 99+% [Gold label]
(Aldrich Chemical Company, Gillingham, Dorset, U.K.)

4.2.2 Investigation of overall migrants from nylon film

A variety of analytical methods have been used to detect and quantify caprolactam and its oligomers in extract and reprecipitated solutions. The simplest is weighing of the solid residue after evaporation of the solvent (gravimetrically). However the presence of foreign matter such as stabilisers and slip agents can lead to inaccurate results. Optical methods are more specific, for example UV and IR spectroscopy (217-219) and refractometry and interferometry (220) have all been used to study oligomers from nylon 6 and nylon 6,6. In this investigation the aqueous extract from the films were studied by UV spectrophotometry and the results compared with conventional gravimetric migration determinations.

4.2.2.1 Experimental methods

Film samples (20 x 10cm) were chopped into 1cm squares and placed in a round bottom flask with 100cm^3 of 18MΩ boiling water. The nylon was boiled under reflux for one hour and the aqueous phase was then removed for analysis.

For gravimetric determinations the aqueous extract was slowly evaporated and the residue collected dried to a constant mass.

Prior to UV examination the aqueous simulant from the migration experiment was cooled and diluted by a factor of twenty. The instrumental parameters employed were as follows :-

INSTRUMENT	:	Pye Unicam SP800 UV/VIS Spectrophotometer
CELL	:	40mm path length [Quartz]
SCAN RANGE	:	200 - 400nm

Suitable calibration graphs were constructed by preparing a range of standard solutions of ε-caprolactam in 18MΩ water. For this work it was assumed that all the oligomers had the same UV response factor.

4.2.2.2 Overall migration results

The aqueous extracts from the nylon films were monitored at 213nm (λ max for ε-caprolactam) after different exposure periods to the boiling water. After an initial one hour boil each film had released migrants corresponding to around 1-2% of the films mass.

For subsequent extraction periods the levels of migrants were found to decrease as would be expected for the progressive removal of residual monomer and oligomers where there is no significant depolymerization. These results are summarised in Figure 4.1.

The results obtained from different measurement techniques are shown in Table 4.1. Conventional gravimetric data is compared with the non-selective UV method and the more accurate results from a calibrated HPLC analysis (for experimental details see Section 4.2.3.2). Within the range of values cited each determination for a different film sample has an error of ± 10%. The range of values obtained may in fact result from variations within the parameter of each films thickness.

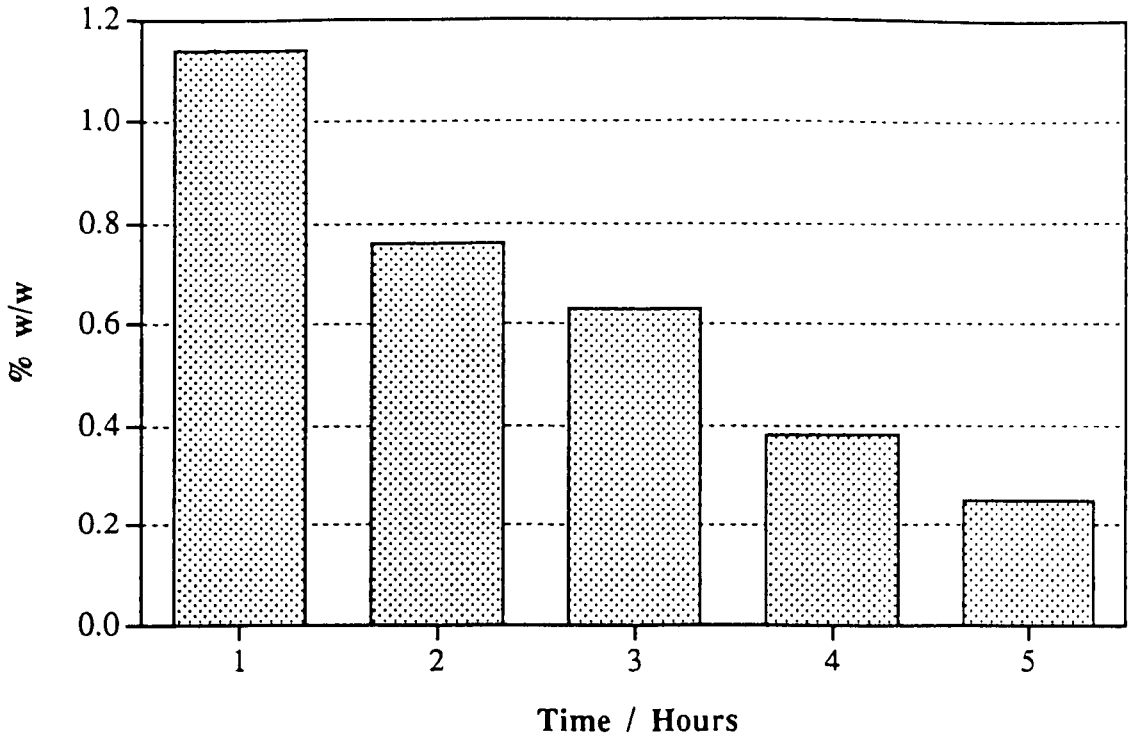


Figure 4.1 **UV analysis of aqueous extract from an 80μm cast nylon 6 film showing the yield of migrants for successive exposure to boiling water for periods of 1 hour.**

Film Thickness / μm	Overall Migration / mg dm^{-2}		
	Gravimetric	UV	HPLC
15	1.0 - 1.6	1.0 - 1.1	1.1 - 1.5
20 +	1.2 - 1.3	*	*
25.4	1.2 - 1.5	1.4 - 1.7	1.2 - 1.6
50	2.2 - 2.8	2.8 - 3.5	2.7 - 3.2
80	3.4 - 4.0	4.1 - 5.1	4.8 - 5.4

* : No data available
\+ : Nylon 6,6 film

NOTE : All samples exposed to boiling water for one hour.
Double sided exposure to simulant.

Table 4.1 **Comparison of overall migration results for nylon films using different measurement methods.**

4.2.3 Investigation of individual migrants from nylon films

Gravimetric and UV analyses are limited because they are unable to identify and quantify the individual migrants from the nylon film. In order to do this some form of separation technique is required. Fractional sublimation (221), paper chromatography (222), gas chromatography (223-225) and gel permeation chromatography (212, 226-228) have been utilized. Although suitable, all of them have some limitations of application, for example:- the higher molecular weight oligomers not subliming, complex extraction procedure, lengthy analysis time and low resolution.

In comparison with the above methods, the introduction of high performance liquid chromatography (HPLC) has brought an appreciable improvement in analysis time and chromatographic separation (211, 229-232).

To characterise the species migrating from the nylon film into an aqueous food simulant mass spectrometry (MS) is used. Mass spectrometry is a powerful tool for providing structural information about the polymer, and several workers have utilised it for oligomer research.

Pyrolysis followed by electron impact (233,234) or chemical ionization (235) has been used to study a series of aliphatic polyamides. At temperatures below 200°C low molecular weight cyclic oligomers can be detected. However if the oligomers are thermally labile or their molecular weight too high, they can not be seen before the thermal degradation of the polymer occurs. To overcome this problem several techniques have been reported, including time of flight secondary ion mass spectrometry (236), and fast atom bombardment (FAB) mass spectrometry (237).

In this investigation the migration of ε-caprolactam and its oligomers into boiling water was studied as a function of time, by analysing the aqueous extracts from the films. Continuous flow frit-FAB LC-MS and direct probe EI-MS methods were used to identify the oligomers and normal and reverse phase HPLC methods with UV detection at 220 and 230nm provided quantitative data.

4.2.3.1 Identification of migrants

The migrants into the aqueous phase were collected as detailed in Section 4.2.2.1. The aqueous phase was rotary evaporated under vacuum at 70°C to approximately 6 cm^3 and then made up to a final volume of 10 cm^3 using methanol / water 80:20 solution. For the liquid chromatography - mass spectrometry (LC-MS) investigations the samples were analysed on a JEOL AX-505WA instrument using the instrumental operating parameters detailed in Table 4.2. This approach was based on a reverse phase methodology Table 4.3 which had been successfully developed for migration studies. The direct probe analyses were carried out on extract samples which had been reduced to dryness leaving a crystalline residue. This residue was subjected to conventional electron impact mass spectrometry using a VG TRIO 3 instrument scanning over the mass range 30 to 600 daltons every second. The sample in the probe tip was rapidly heated to 200°C and several mass spectra were recorded during the sample volatilization.

On volatilization of the dried nylon 6 residue sample the presence of ions m/z 113, 226, 339 and 452 was observed (Figure 4.2), indicating the presence of caprolactam and its dimer, trimer and tetramer. Analysis of the nylon 6,6 (Figure 4.3) residue failed to show the presence of anything larger than the cyclic monomer (m/z 226). The absence of larger ions corresponding to larger oligomers may result from either a lack of volatility or thermal instability under the mass spectrometers operating conditions.

The advantage of LC-MS techniques over electron impact mass spectrometry is that they do not rely on the volatility of the individual components to lead to separation. Therefore it is not restricted like electron impact to the analysis of low molecular weight oligomers. The LC-MS analyses of the aqueous extracts from nylon 6 films produced a chromatogram as shown in Figure 4.4. Positive ion fast atom bombardment (FAB) mass spectra of the individual peaks eluting indicated the presence of protonated molecular ions of the caprolactam oligomers from the monomer to the nonamer (i.e. m/z $114+n \times 113$;$n = 0$ to 8). Which suggests that all these species are cyclic in nature; for linear species the protonated molecular ions would have been m/z 132, 245, 358 etc.

It was also noted that under the reverse phase conditions the dimer eluted before the monomer.

Instrument

MS	JEOL AX - 505WA
HPLC	HP - 1090L

MS Conditions

Acceleration voltage	3KV
Ionization	FAB
Polarity	Positive
Scan range	50 - 1500
Scan speed	5 s

HPLC Conditions

Column	Capcellpak ODS (4.6mm i.d. x 150mm)
Eluent	A = Water : B = Methanol
	B = 20% at 0 min to
	B = 70% at 25 min.
	Linear gradient
Flow	$1cm^3\ min^{-1}$
Column temperature	40°C
UV detector wavelength	230nm
Injector volume	100µl

FAB Conditions

Neutral gas	Xe
Gun potential	4KV
Matrix	3% Glycerol / Methanol
	($0.3cm^3\ min^{-1}$ post column addition)

Table 4.2 Experimental conditions for liquid chromatography - mass spectrometry (LC-MS) analyses.

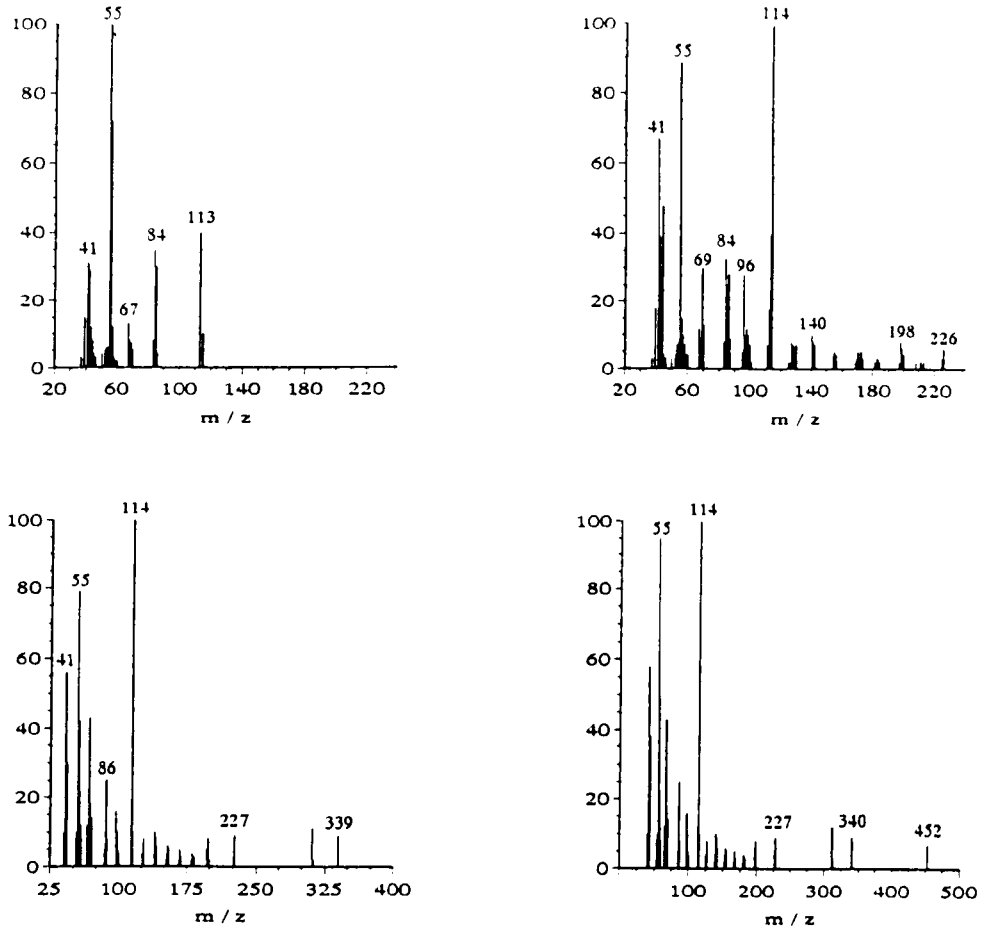


Figure 4.2 **Selected mass spectral data obtained from the direct probe analyses of the dried residue from the extraction process. In this case conventional electron impact ionization shows molecular ions at m/z 113, 226, 339 and 452 (n=1, 2, 3 and 4) for nylon 6 films.**

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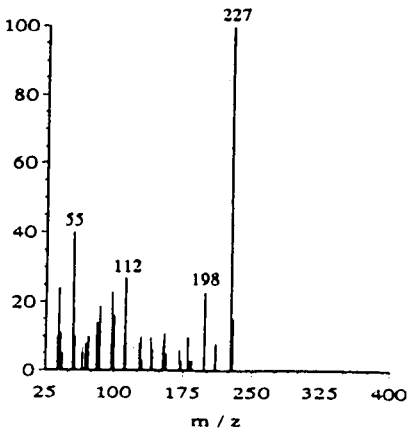

Figure 4.3 **Mass spectral data obtained from the direct probe analyses of the dried residue from the extraction process of nylon 6,6 film.**

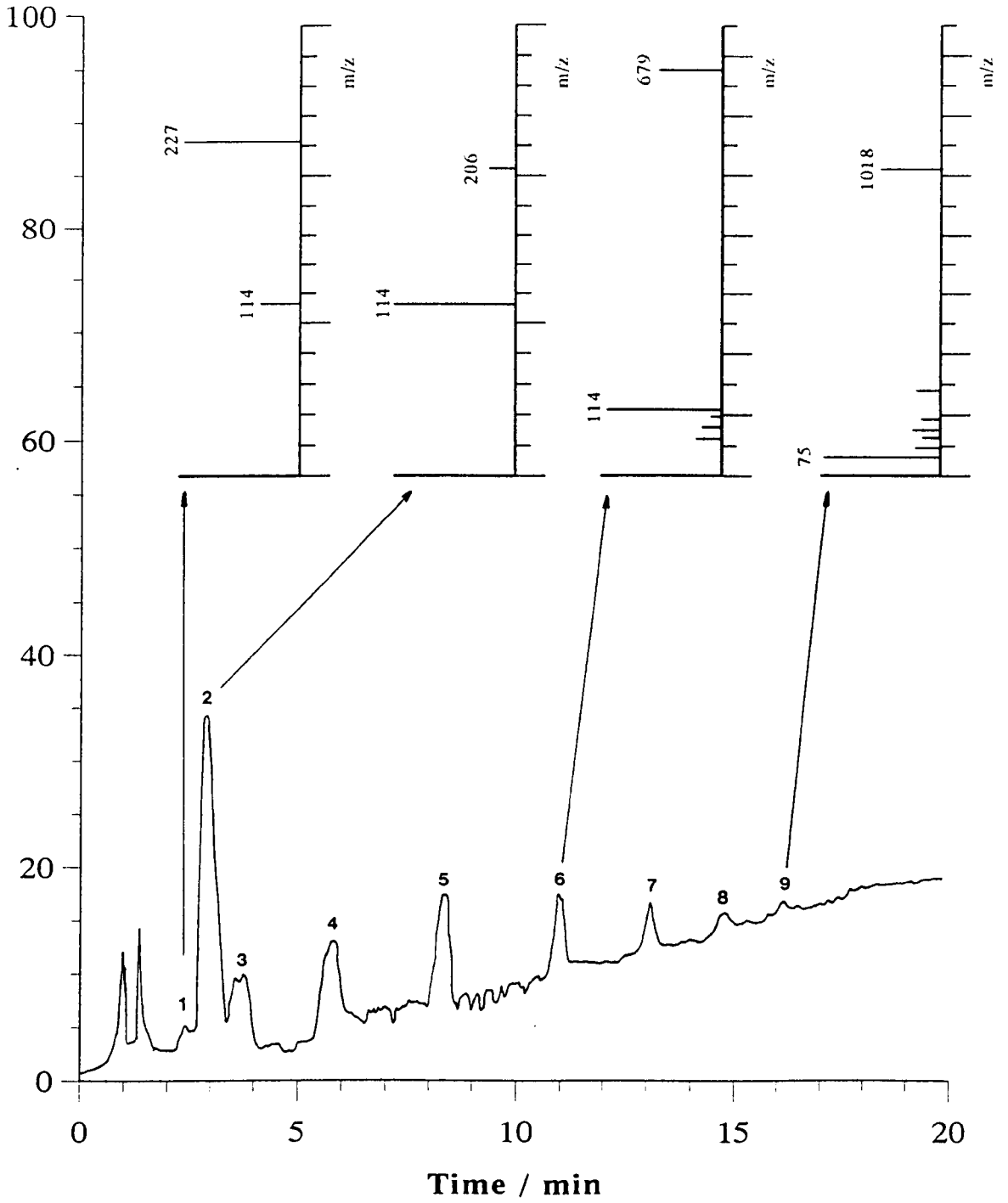

Figure 4.4 **Composite trace for the LC-MS data. Mass spectra for individual peaks in the UV trace are shown as inserts. The mass spectra show the protonated molecular ions of the oligomers n=1, n=2, n=6 and n=9.**

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4.2.3.2 Quantification of migrants

Both normal and reverse phase HPLC analysis with UV detection were used to quantify the migration of the individual oligomers. The aqueous extract was prepared as specified in Section 4.2.2.1 and rotary evaporated under vacuum at 70°C to a volume of approximately 6 cm^3. This solution was then made up to a final volume of 10cm^3 using acetonitrile / water 90:10 prior to analysis.

The individual instrumental analytical conditions are detailed in Table 4.3 and in both cases calibration curves were prepared to determine the limits of detection of each method.

		Normal phase	**Reverse phase**
Eluent	:	Acetonitrile : Water 82 : 18	Methanol : Water 45 : 55
Flow rate	:	1.5cm^3 min^{-1}	1.5cm^3 min^{-1}
Pump	:	Pye Unicam PU4015	Pye Unicam PU4015
Injector:		Marathon Autosampler 100µl sample loop at ambient temperature	Marathon Autosampler 100µl sample loop at ambient temperature
Column	:	Partisil 5µm silica 250 x 4.6mm i.d. Whatman International Ltd. Maidstone, UK.	Alphasil 5µm ODS C_{18} 250 x 4.6mm i.d. HPLC Technology Ltd. Macclesfield, UK.
Detector	:	Pye Unicam PU4025 UV at 220nm	ACS Model 750/11/AZ UV at 230nm
Integrator	:	Pye Unicam PU4810	Hewlett Packard HP3394A

Table 4.3 Summary of HPLC experimental conditions

The caprolactam and oligomer levels in the films were determined using the following equations based on external standard calibration methods.

$$\text{Concentration of oligomers } (\mu g\ dm^{-2}) = \frac{A_{SPL}}{RF} \times \frac{W_{STD}}{A_{STD}} \times \frac{1}{A_{NY}}$$

$$\text{Concentration of oligomers } (\mu g\ g^{-1}) = \frac{A_{SPL}}{RF} \times \frac{W_{STD}}{A_{STD}} \times \frac{1}{W_{NY}}$$

$$\text{Concentration of oligomers } (\%) = \frac{A_{SPL}}{RF} \times \frac{W_{STD}}{A_{STD}} \times \frac{100}{W_{NY}}$$

Where :-

A_{SPL} = Peak area of oligomer peak

A_{STD} = Peak area of ε-Caprolactam used as external standard

W_{STD} = Mass (g) of ε-Caprolactam used as external standard

A_{NY} = Area (dm^2) of nylon film in contact with food simulant

W_{NY} = Mass (g) of nylon film extracted

RF = Response factor at 220nm for specific cyclic oligomers

The individual response factors have been determined by Bonifaci et al. (211) and Sedgwick (209) and are shown in Table 4.4.

Oligomer	Sedgwick	Bonifaci
n = 1 ε-Caprolactam	1.00	1.00
n = 2	0.25	0.32
n = 3	0.30	0.30
n = 4	0.33	0.30
n = 5	0.30	0.30
n = 6	0.33	-
n = 7	0.33	-
n = 8	0.33	-

Table 4.4 Response factors for individual cyclic oligomers of nylon 6

Chromatograms obtained from the normal and reverse phase analyses of the caprolactam oligomers are compared in Figure 4.5. These chromatograms demonstrate the change in elution order for the small peak identified as 2, the dimer.

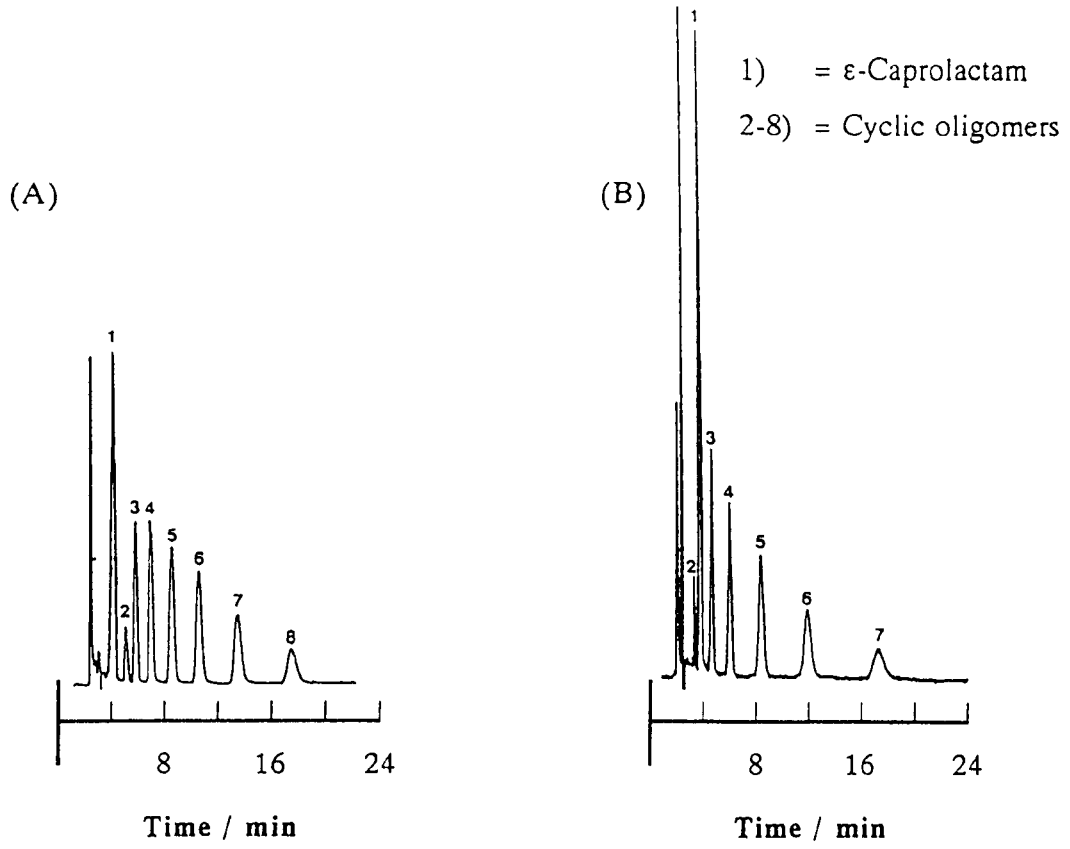

Figure 4.5 **Typical HPLC chromatogram obtained for the separation of caprolactam and its oligomers from aqueous extracts of nylon 6. Using (A): normal phase (B): reverse phase columns and conditions.**
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Calibration exercises showed both HPLC approaches to be suitable, the normal phase conditions being subject to a minimum detection limit of 50μg dm^{-3}. This method was used to determine the yield of oligomers (n = 1 - 8) that had leached into the water after boiling the film for one hour. Comparison between the sets of data in Table 4.5 indicates that there were some differences between cast and oriented films. The overall yield for the cast films were very similar at 0.9 -1.1% w/w, but the oriented value is slightly larger at 1.5% w/w. In addition there were some differences in the ratios of the yields of the different oligomers between the two film types. As can be seen in Figure 4.6 a higher yield of the larger cyclic oligomers from the oriented film is observed compared with the cast film.

Compound		Amount / μg dm^{-2}			
		Oriented	Cast		
		15μm	25.4μm	50μm	80μm
n = 1 ε-Caprolactam		160	80	930	1000
n = 2		55	60	150	180
n = 3		240	290	510	815
n = 4		210	305	540	835
n = 5		250	290	480	655
n = 6		170	180	295	380
n = 7		130	55	90	130
n = 8		100	10	30	70
Polymer film	/ g dm^{-2}	0.18	0.29	0.56	0.86
ε-Caprolactam	/ mg dm^{-2}	0.2	0.1	0.9	1.0
Oligomers	/ mg dm^{-2}	1.2	1.2	2.1	3.1
Total	/ mg dm^{-2}	1.4	1.3	3.0	4.1
Total	/ % w/w	1.49	0.89	1.09	0.94

Results are subject to a ± 10% variation

Table 4.5 Yield of caprolactam and oligomers migrating from chopped nylon 6 film into boiling water after one hour.

It should be noted that the films differ in thickness and that the migration rates of individual oligomers would be different. It was therefore important to determine the migration time after which no detectable change could be observed. This was carried out by extracting film samples repeatedly for three periods of twenty minutes and then for three periods each of one hour. After each extraction the water was removed, analysed and replaced with fresh hot millipore water to continue the investigation.

The results obtained (Figure 4.7) show that for thin film (15μm) the majority of the oligomers being considered had been removed by boiling for twenty minutes, the typical preparation time for a boil in the bag meal. As anticipated from a migration model based on diffusion, the thicker the film the greater the time period for extraction to reach a maximum level. For the 80μm film up to four hours of extraction was required for oligomers larger than the pentamer. These results were readily reproducible for the same film and showed that the film thickness has a significant effect on the migration characteristics of materials.

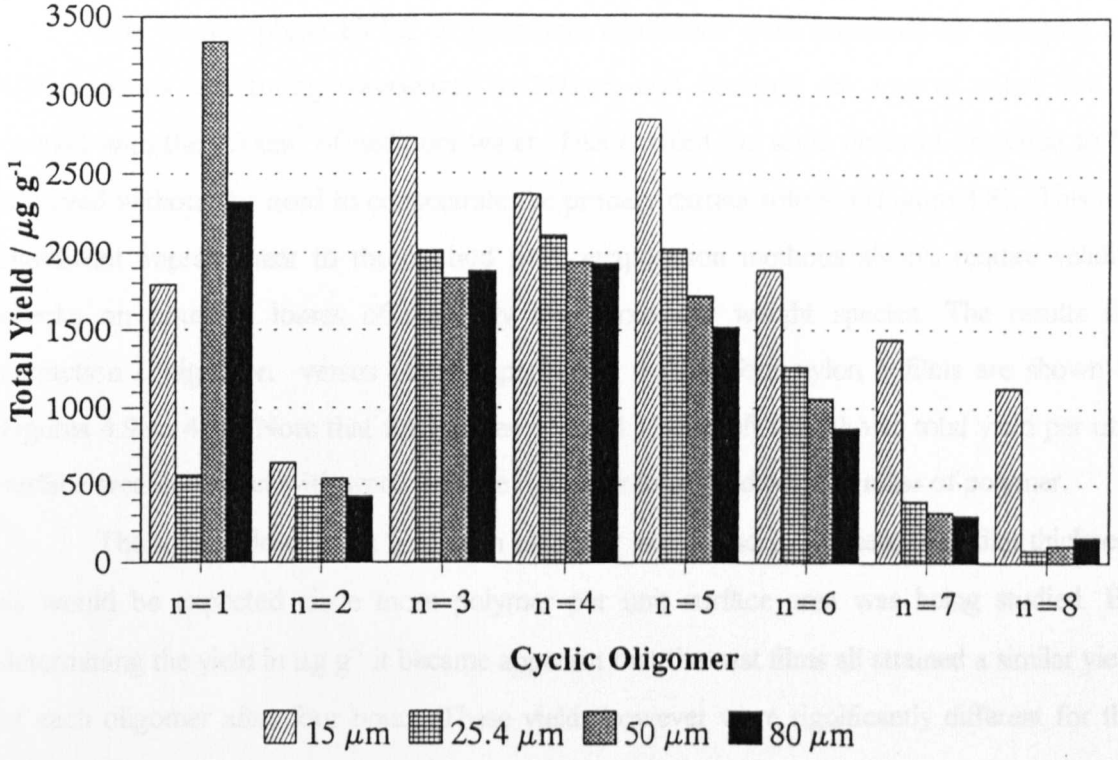


Figure 4.6 **Comparison of the yields of caprolactam and oligomers migrating into boiling water after one hour.**

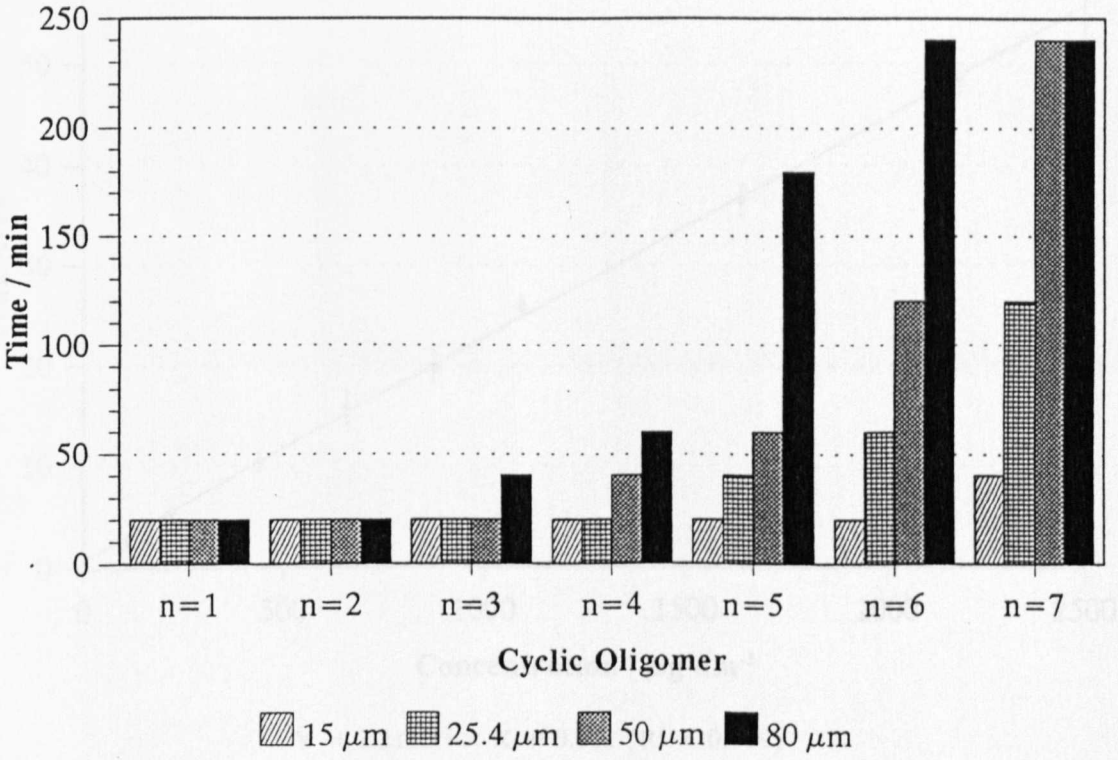


Figure 4.7 **Time taken for complete extraction of the available caprolactam and oligomers from nylon 6 films using boiling water.**

The reverse phase HPLC experimental conditions were improved by changing the UV detectors monitoring wavelength to 220nm, and doubling the area of nylon film in contact with the $100cm^3$ of millipore water. This enabled the same limits of detection to be achieved without the need to concentrate the primary extract solution (Figure 4.8). This is a significant improvement to the method since evaporation methods always require validity checks on potential losses of relatively low molecular weight species. The results for extraction / migration versus time experiments for the four nylon 6 films are shown in Figures 4.9 to 4.12. Note that for Figures 4.9 to 4.12 the left axis shows total yield per unit surface area in contact with water and the right axis total yield per unit mass of polymer.

The total yield ($\mu g\ dm^{-2}$) of each oligomer was found to increase with film thickness as would be expected since more polymer per unit surface area was being studied. By determining the yield in $\mu g\ g^{-1}$ it became apparent that the cast films all attained a similar yield of each oligomer after four hours. These yields however were significantly different for the oriented film.

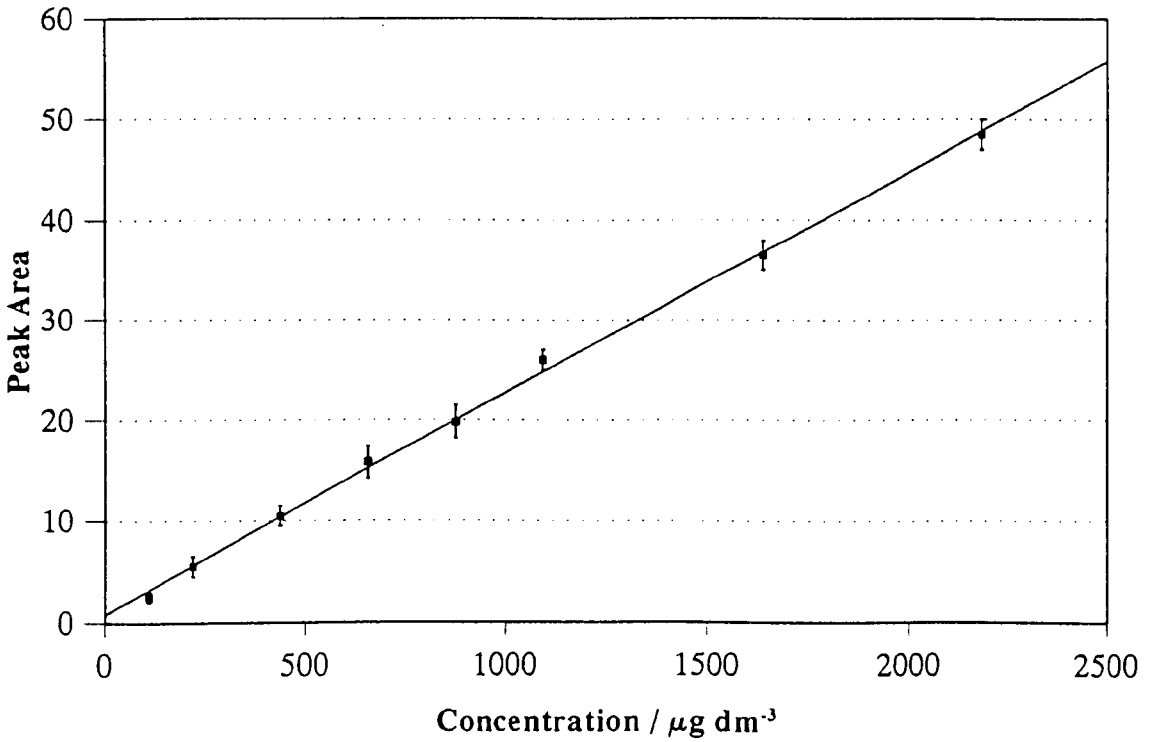


Figure 4.8 Calibration data for caprolactam in water

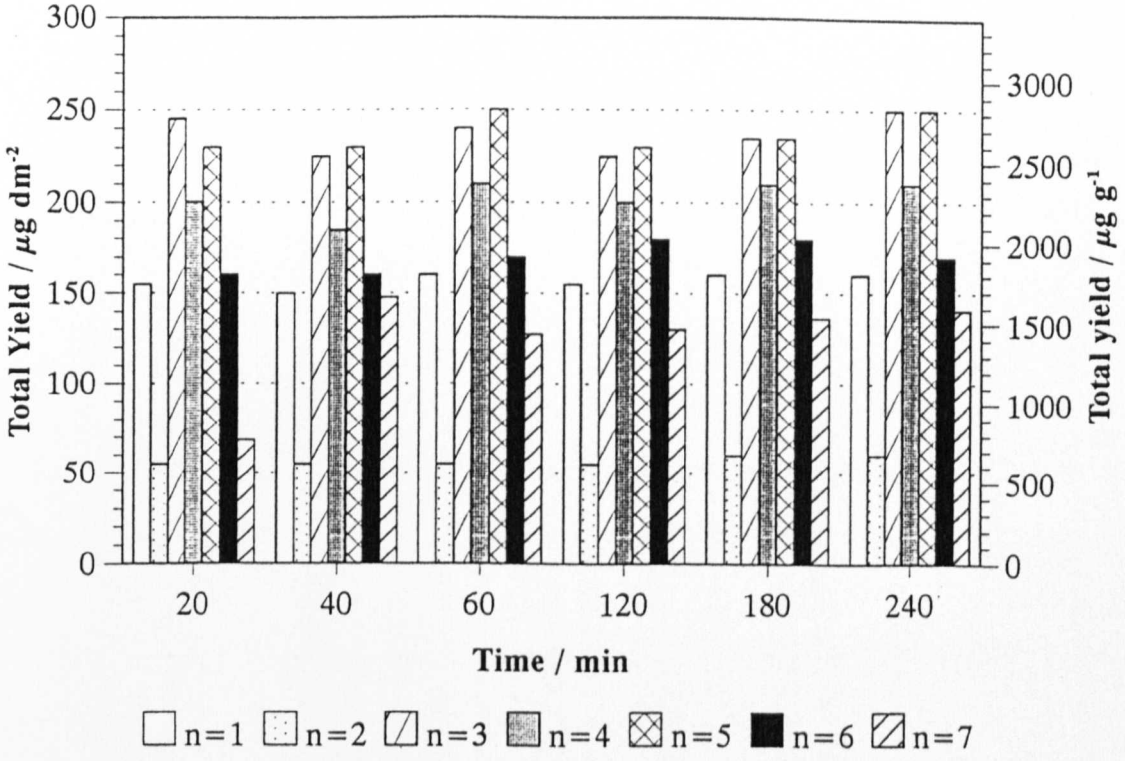


Figure 4.9 **Comparison of the yields of different oligomers from 15μm oriented film as a function of extraction time into boiling water.**

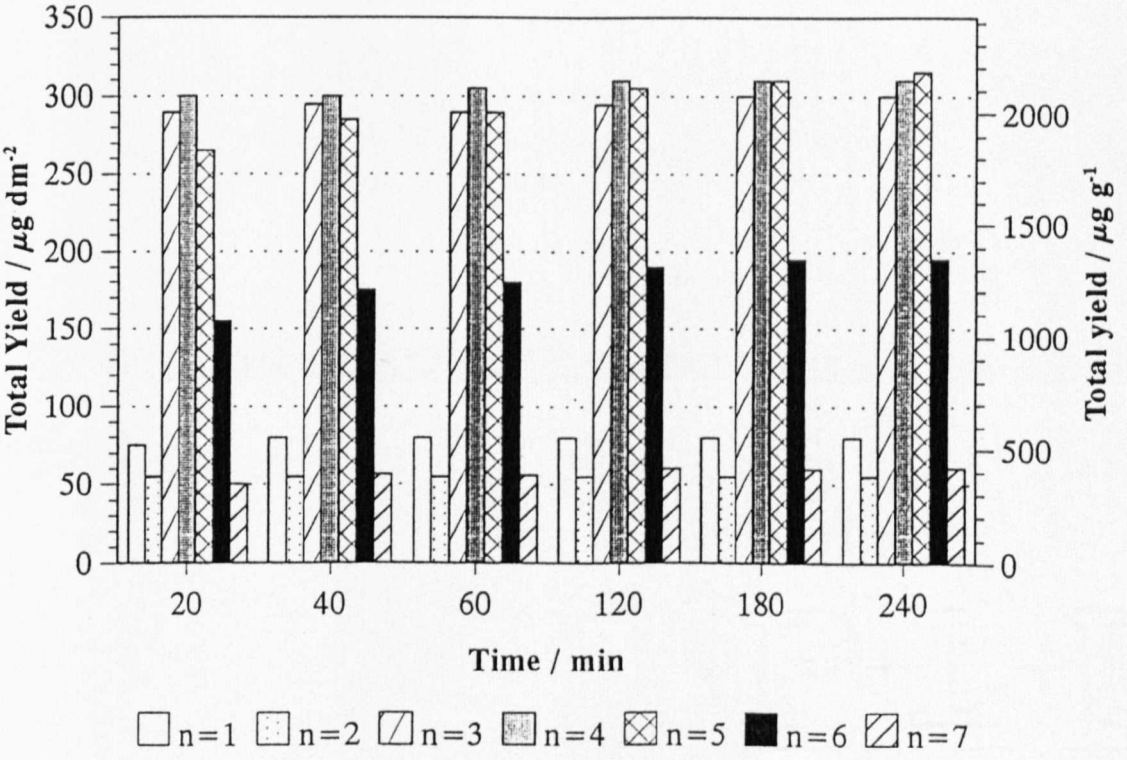


Figure 4.10 **Comparison of the yields of different oligomers from 25.4μm cast film as a function of extraction time into boiling water.**

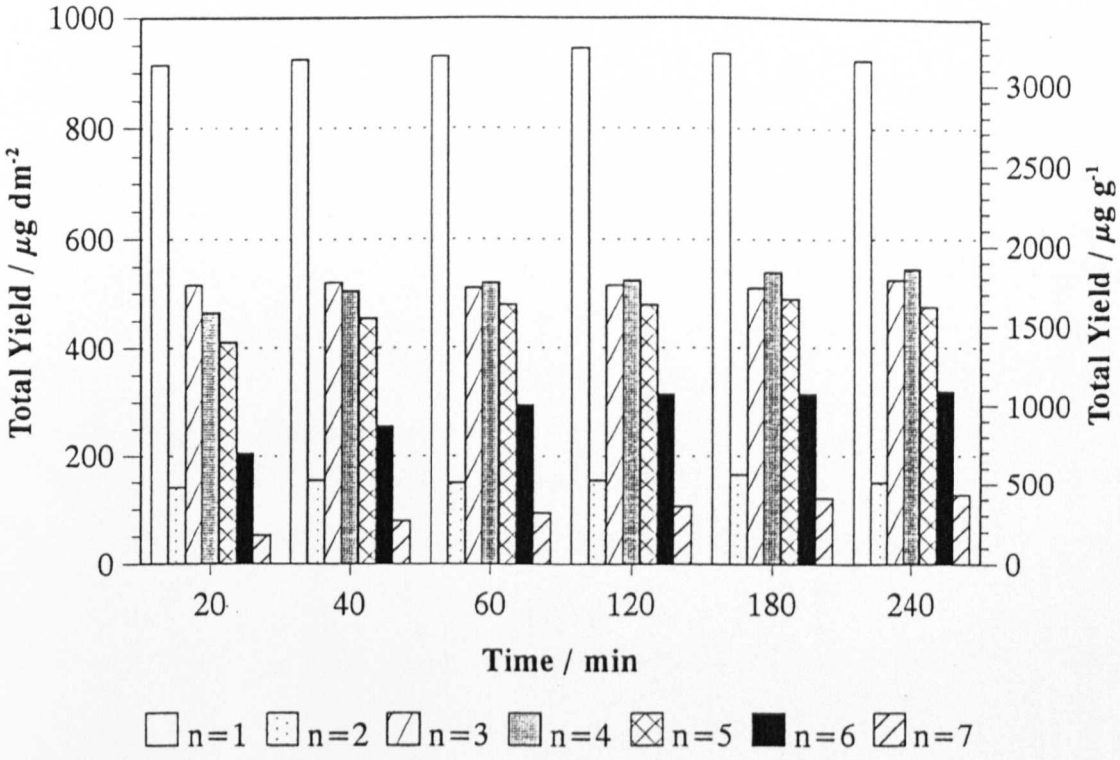


Figure 4.11 **Comparison of the yields of different oligomers from 50μm cast film as a function of extraction time into boiling water.**

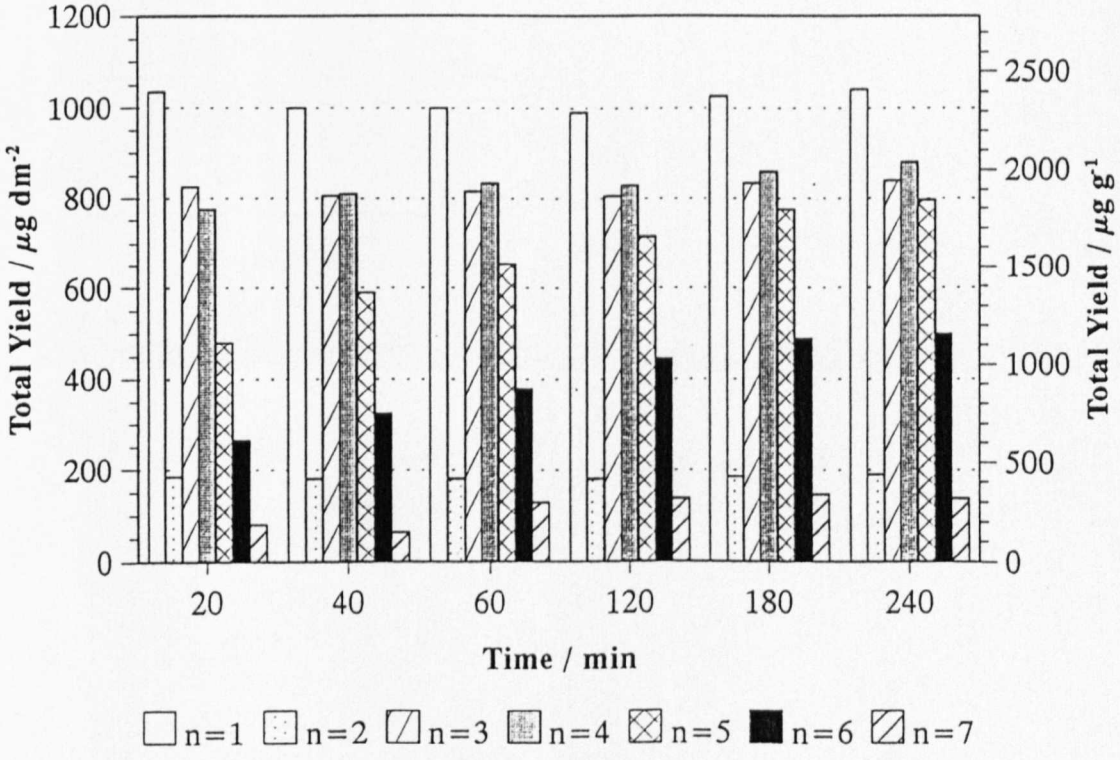


Figure 4.12 **Comparison of the yields of different oligomers from 80μm cast film as a function of extraction time into boiling water.**

4.3 SUMMARY

This work has confirmed the presence of caprolactam and its cyclic oligomers (up to the nonamer) in water boiled in contact with food grade nylon 6 and also the cyclic monomer in nylon 6,6. The results may be significant in terms of migration from food packaging into the food simulant given the loss in weight 1.0 - 1.5% w/w. The largest loss being observed for the oriented film, suggesting that the type of film used has some bearing on the total yield of migrants. In addition the ratios of the individual oligomers produced from the oriented film upon extracting the nylon 6 film for four hours were significantly different to the cast films.

As anticipated thicker films produced greater mass of migrants and required longer extraction times for complete removal of residual oligomers. The thickest film (80μm) requiring up to four hours extraction which greatly exceeds normal cooking periods.

Despite a change in elution order for the oligomers when analyzed under different conditions the LC-MS data confirmed the presence of cyclic oligomers with no other materials from the nylon being identified to be present in the aqueous extract.

In normal everyday use the food within a boil in the bag product is separated from the nylon by a layer of polyolefin and adhesive. Therefore the significant levels of oligomers found to be migrating from the nylon film would be contained within the water surrounding the boil in the bag pouch. These results do however become important if part of the meal is cooked in the water surrounding the pouch.

CHAPTER 5 : POLYURETHANE ADHESIVES

5.1 INTRODUCTION

In Europe the majority of boil in the bag food packaging is usually constructed from an outer film of polyamide and an inner film of polyethylene bonded together with a polyurethane adhesive to produce a laminate. The polyurethane adhesive is the most complex component of the laminate structure since it will contain many of the materials specified in Table 5.1.

Polyurethane adhesives are available as both one and two component systems. For high performance laminates where barrier properties are critical a two component highly cross-linked adhesive is usually employed. Two component adhesive systems consist of a polyisocyanate, or isocyanate terminated polymer of molecular mass less than 2000 dissolved in a solvent such as methyl ethyl ketone or ethyl acetate. This is then reacted with a hydroxyl terminated polyether or polyester of molecular mass 2000-5000 also dissolved in a solvent. The adhesive formulation is then applied to the most heat resistant and solvent resistant of the laminate films; in this case nylon, using a roller. Any excess solvent is then removed in a vented oven and the base film is then combined with the polyethylene using a nip roller at a temperature of 70°C to complete the lamination.

The amount of adhesive required varies from about 2 to 8g m^{-2} depending on the type and application of the laminate. Simple lamination of plain plastic films requires 2 to 3g m^{-2}, printed film 3 to 5g m^{-2}, and higher coating weights are required for heated or sterilisable laminates. An adhesively bonded laminate is therefore an extremely complex material (see Table 5.2) requiring an understanding of the components typically used in current food grade applications.

5.1.1 Isocyanates

The true foundation of the polyurethane industry is the isocyanate. Isocyanates are compounds containing an NCO group attached to an organic entity. They were first prepared by Wuitz in 1849, but their full commercial potential was not recognised until 1937 when Bayer and co-workers produced the first polymer. Many different chemical reactions of organic isocyanates have been described in the chemical literature over the past 40 years (239-240) and most of these have been exploited for the synthesis of polymeric materials.

COMPONENTS	PROPERTIES
DIISOCYANATES	
4,4'-MDI 4,4'-methylenebis (phenyl isocyanate) + variants (polymerized or isomer blends)	Good toughness Good reactivity Cost effective Low vapour pressure
Isophorone diisocyanate (IPDI) 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate	Polyurethane's have good solubility Good light stability Intermediate vapour pressure Very expensive Very slow reactivity
Hexamethylene diisocyanate (HDI) 1,6-diisocyanato-hexane	Polyurethane's have good solubility Good light stability High vapour pressure Very expensive Moderate reactivity
POLYOLS	
Polyether Polyols	Cost effective Good plastic adhesion Poor metal and PET film adhesion
Polyester Polyols (based on aliphatic di-acids)	Good plastics adhesion Moderate metal and PET adhesion Moderate cost
Polyester Polyols (based on mixed aliphatic/aromatic di-acids)	Good plastics, metal and PET adhesion Moderate to high cost
ADDITIVES	
Epoxy resins	Heat stability and chemical resistance
Silanes	Chemical resistance
Oleamide + Erucamide	Modifies slip characteristics of laminates
Acids (benzoyl chloride, phosphoric acid)	Controls reaction rate, stabilises
Antioxidants	Improves colour stability
Catalysts (dibutyl tin dilaurate)	Increases reaction rate
OLIGOMERS	From polyester resins and polyether polyols

Table 5.1 Possible components of polyurethane laminating adhesives

Type 1 for Nylon 6,6 / Adhesive / LLDPE

Polyester components

Adipic acid

Isophthalic acid

Diethylene glycol

Ethylene glycol

4,4'-MDI

Uretonimine

Polycarbodiimide

Phosphoric acid

Type 2 for Nylon 6 / Adhesive / LLDPE

Polyether components

Glycerol

Propylene oxide

Ethylene oxide

4,4'-MDI

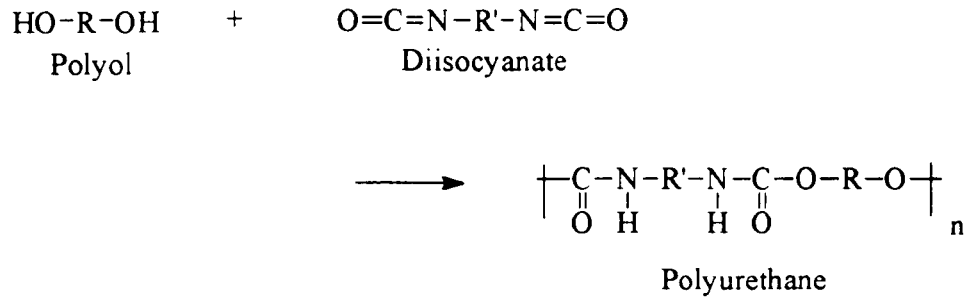
2,4'-MDI

2,2'-MDI

Table 5.2 Typical examples of the formulation of some polyurethane based adhesives for laminating applications

Di- and polyfunctional isocyanates are now used to produce the polymers required for the production of foams, coatings, fibres and adhesives.

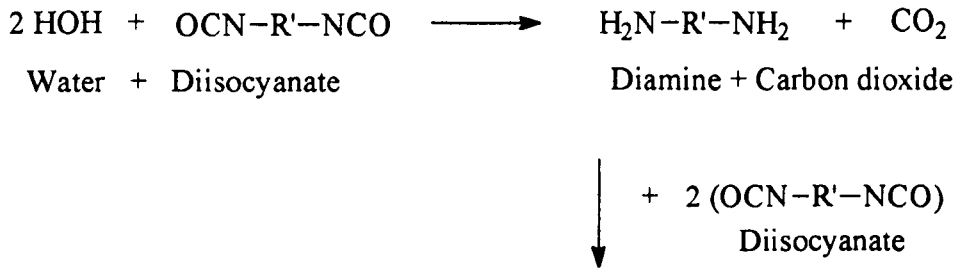
The most important reaction in today's polyurethane adhesives industry is the addition reaction between di- or polyfunctional isocyanates and di- or polyfunctional hydroxyl compounds (polyols), such as hydroxyl-terminated polyethers or polyesters (241). When only difunctional reactants are used, linear polyurethanes are produced, as shown in the following page.

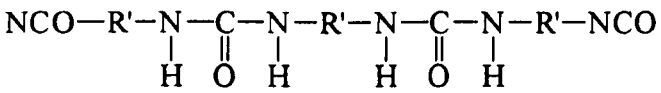


Polyurethane

These polyurethane polymers tend to be soft with a high degree of elongation. However, if the functionality of the hydroxyl or isocyanate component is increased to three or more, branched or cross-linked polymers are formed, and these tend to be more rigid.

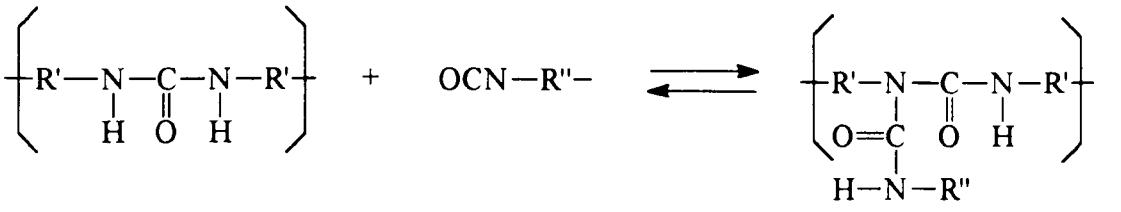
The second most important reaction of isocyanates is with water to produce carbon dioxide, a diamine and ultimately a polyurea based polymeric system. This sequence of reactions is principally used in the production of low density flexible foams, but similar reactions can occur in the presence of atmospheric moisture.



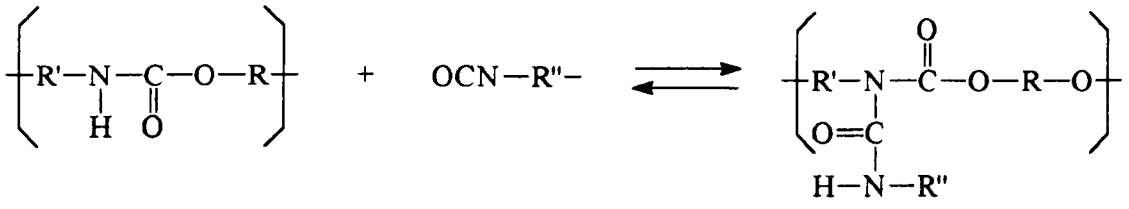


Diisocyanatopolyurea

Isocyanate groups react with any compound containing 'active' hydrogen atoms and diisocyanates can therefore be used to produce polymers as detailed above. However, if the ratio of isocyanate to isocyanate reactive mixture is increased and an excess of isocyanate groups is used this will tend to promote secondary reactions. Leading to the formation of biuret and allophanate linkages as the isocyanates react with the active hydrogens on the urethane and urea linkages. Both reactions are cross-linking reactions and this ultimately results in a more rigid, and thermally stable adhesive.



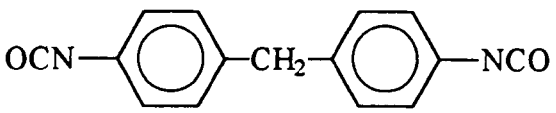
Urea Isocyanate Biuret



Urethane Isocyanate Allophonate

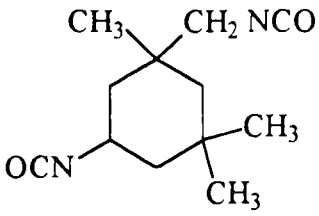
At one time toluene diisocyanate was the most common diisocyanate used in the production of polyurethane adhesives for laminates. However, toluene diisocyanate has a high vapour pressure and is a respiratory irritant and lachrymator. Prolonged inhalation of toluene diisocyanate vapours was found to lead to symptoms resembling asthma as well as to sensitisation of the person working with toluene diisocyanate. As a result of the toxic nature of this volatile compound the market is now predominantly MDI based, due to MDI having a much lower vapour pressure.

When this work was undertaken (1990-93) the diisocyanates most commonly used in the lamination of European packaging films were in decreasing order of volume used :-



4,4'-MDI

4,4'-methylenebis (phenyl isocyanate)



Isophorone diisocyanate or IPDI

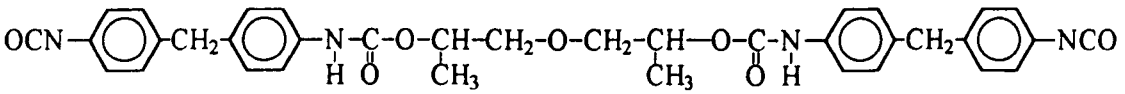
3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate

$$OCN-(CH_2)_6-NCO$$

Hexamethylene diisocyanate or HDI

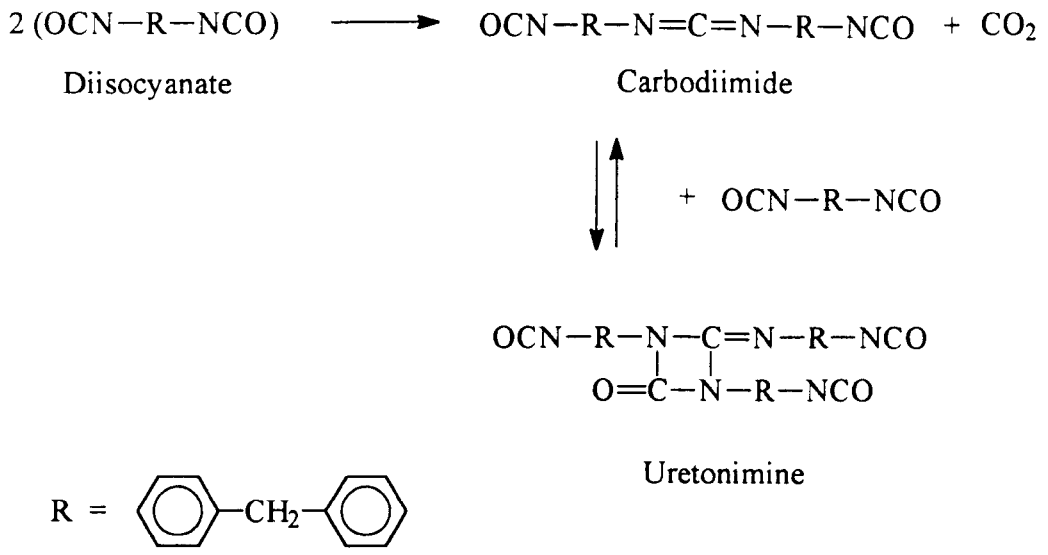
1,6-diisocyanato-hexane

Pure MDI is a white to pale yellow solid of melting point about 38°C with a tendency to form insoluble dimers and trimers when stored (242). The difficulty of handling solid pure MDI and its increased tendency to produce a dimer when stored as a liquid above 40°C, has led to the development of modified pure MDI's which are liquids at ambient temperatures and have a reduced tendency to dimerise. Two main methods of depressing the melting point of pure MDI are used. Both methods involve reacting part of the pure MDI to form a derivative that is soluble in the parent monomer. One method is to react some of the isocyanate groups with an aliphatic diol of low molecular mass or with a mixture of such diols to yield a solution of diurethanes having isocyanate end groups in 4,4'-MDI.



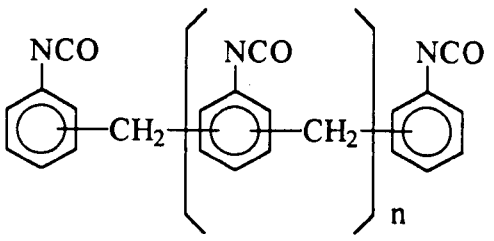
Modified pure MDI

The second common method of modifying pure 4,4'-MDI is by converting some of the diisocyanate to give a uretonimine.



Another method utilized by the adhesives industry to reduce the melting point of pure 4,4'-MDI is to increase the content of its isomers 2,2'- and 2,4'-MDI in the mixture. Compositions containing too much of these isomers lead to adhesives with a very high modulus, which is not desirable, but adjustment of the proportion of these isomers to the correct level is useful method of increasing the storage stability and liquidity of MDI (241).

In recent years 'crude' isocyanates, undistilled grades of MDI have also found extensive use in the manufacture of adhesives. Polymeric MDI as it is sometimes called is prepared by the phosgenation of aniline-formaldehyde condensates. The resulting viscous liquid has the benefit of a lower vapour pressure and greater number of reaction sites than pure MDI (242).



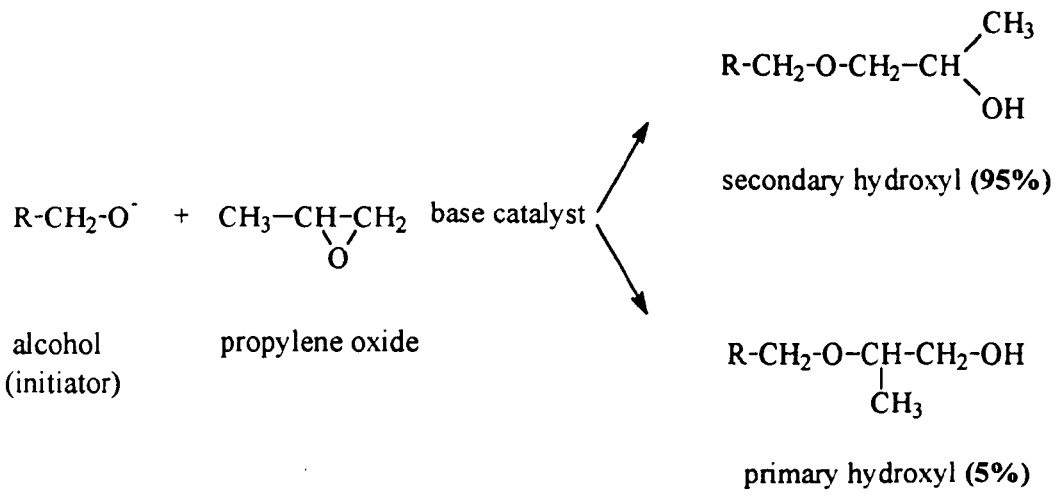
Polymeric MDI

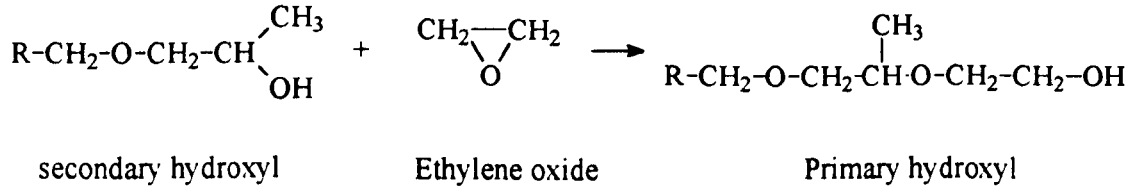
MDI is the principal aromatic diisocyanate used in the production of polyurethane adhesives, primarily due to the raw material being relatively inexpensive. The aliphatic diisocyanates HDI and IPDI are more expensive and tend to react more slowly during the polymerization process. However, to increase the polymerization rate metal catalysts are

added, and the reaction is sometimes initiated by small amounts of aromatic diisocyanates. Despite the increased cost of these types of polyurethane adhesives they are now becoming more popular. This is because polyurethane adhesives produced using aliphatic diisocyanates have two major advantages over their aromatic counterparts; they are less prone to heat degradation and discoloration.

5.1.2 Polyols

A wide range of polyols are used in polyurethane manufacture, but most fall into two classes : hydroxyl terminated polyethers, or hydroxyl terminated polyesters. The structure of the polyol plays a large part in determining the properties of the final polyurethane adhesive. Polyesters are generally more expensive than polyethers but tend to have superior physical properties and thus both polyol types are used.





Hydroxyl terminated polyethers are produced by the addition polymerization of alkylene oxides; usually polypropylene oxide, in the presence of an alcohol or amine which acts as an initiator. Under commercial polyol production the addition polymerization is base

catalysed. The basic conditions cause the epoxide ring of the polypropylene oxide to open preferentially at the less sterically hindered position, giving predominantly secondary hydroxyl groups. However, secondary hydroxyl groups are several times less reactive with isocyanates than primary hydroxyl groups. Therefore the primary hydroxyl content is increased by the preparation of a block copolymer with an oxyethylene tip by the separate reaction of a mixture of ethylene oxide and polyoxypropylene polyols. By this means the percentage of primary hydroxyl groups can be varied from 5 to 80% of the total hydroxyl end groups. On completion of the above reactions the low molecular weight oligomers are stripped off and the resultant product, which may range from an oily product to a wax like material is retained.

Both aromatic and aliphatic polyesters with terminal hydroxyl groups are used to make polyurethane adhesives. Polyester polyols tend to be more expensive than polyether polyols due to the higher cost of the raw materials and longer reaction time. Consequently they are only used to make polyurethanes for demanding applications where the particular physical properties obtainable from polyesters are important. Polyester based adhesives combine high levels of tensile properties with good resistance to flexing and many types of oil. They are also less easily oxidised and resist higher temperatures than polyethers.

Polyesters are produced by the condensation reaction between glycols and diffunctional carboxylic acids. By the addition of a small amount of triol to the reaction mixture branching can be introduced. This leads to urethanes with greater heat and chemical resistance. Of the range of acids and glycols which are readily available (see Table 5.3), adipic and isophthalic acids have been extensively utilized in conjunction with either ethylene or diethylene glycol.

The required acids and glycols are heated together in a resin kettle and as the esterification proceeds the air and water is removed by a slow stream of nitrogen passing through the mixture. After about 75% conversion the reaction becomes very slow and many hours are required before completion is approached. When prepared the polyesters are mixtures of species with moderately high molecular weight which can not be easily purified by recrystallisation or distillation. Therefore, the low molecular weight oligomers and water liberated during the reaction are removed by vacuum stripping.

Carboxylic acids

Name	Structure	Functionality
Adipic	$HO_2C(CH_2)_4CO_2H$	2
Sebacic	$HO_2C(CH_2)_8CO_2H$	2
Phthalic (anhydride)	$C_6H_4(CO)_2O$ *ortho*	2
Isophthalic	$C_6H_4(CO_2H)_2$ *meta*	2
Terephthalic	$C_6H_4(CO_2H)_2$ *para*	2

Glycols

Name	Structure	Functionality
Ethylene glycol	$HO{\bullet}CH_2{\bullet}CH_2{\bullet}OH$	2
Diethylene glycol	$HO{\bullet}(CH_2)_2{\bullet}O{\bullet}(CH_2)_2{\bullet}OH$	2
1,2-Propylene glycol	$HO{\bullet}CH_2{\bullet}CHMe{\bullet}OH$	2
1,4-Butanediol	$HO{\bullet}(CH_2)_4{\bullet}OH$	2
Neopentyl glycol	$HO{\bullet}CH_2{\bullet}CMe_2{\bullet}\ CH_2{\bullet}OH$	2
Trimethylolpropane	$EtC(CH_2{\bullet}OH)_3$	3

Table 5.3 Raw materials available for polyester production (241)

5.1.3 Toxicological and legislative aspects

Polyurethane adhesives are produced by the reaction between polyfunctional isocyanates and polyfunctional hydroxyl compounds (polyols). These polyfunctional hydroxyl compounds can be hydroxyl terminated polyethers or aromatic / aliphatic polyesters. Ethylene oxide and propylene oxide which are the two main monomers used in the production of hydroxyl terminated polyethers have been assessed by the Scientific Committee for Food (SCF) (26). No acceptable daily intake or tolerable daily intake has been established but their present use in plastics intended to come into contact with foodstuffs, is acceptable. However, they have both been shown to be mutagenic in several studies (243), inducing tumours in rats after oral administration. Directive 90/128/EEC also states that the maximum permitted quantity of ethylene oxide and propylene oxide in the final article should not exceed 1mg kg^{-1} (20).

The other main monomers used in the production of hydroxyl terminated polyesters have also been assessed by the committee. Both ethylene glycol and diethylene glycol have been accepted for use in food contact materials and a tolerable daily intake of 0.5mg kg^{-1} body weight has been established (26). In addition, according to the list of authorised monomers and other starting materials laid down in directive 90/128/EEC,

they both have a specific migration limit into food or food simulant of 30mg kg^{-1} (20). Two of the dicarboxylic acids, namely adipic and isophthalic, which are used in the production of polyesters were examined. The adipic acid has been accepted for use in food contact materials and an acceptable daily intake of 5mg kg^{-1} has been estabilised (26). However, isophthalic acid has been assessed by the SCF but inadequate data was available for the committe to express an opinion.

The main hazard associated with isocyanates, is the inhalation of vapour. This leads to respiratory problems and can result in sensitization of the person working in the isocyanate vapour. The National Institute for Occupational Safety and Health (NIOSH) has assessed these hazards and recommended a time weighted average (TWA) exposure of 20ppb for any 10 minute period or 5.8ppb for any 8 hour period, for all organic diisocyanates (244). The relative hazard from an isocyanate, varies widely with the volatility of that particular isocyanate and the temperature at which it is used. Modified or polymeric MDI's are liquids at ordinary temperatures and therefore have a low vapour pressure which reduces the hazard.

The residual levels of monomeric isocyanate found in laminating adhesives are very low and therefore the hazard to human health is minimal. The present use of HDI and MDI in plastic materials which are intended to come into contact with foodstuffs has been assessed by the SCF and has been found to be acceptable (26). With regards to determining an acceptable and tolerable daily intake for each of the monomers the SCF were unable to reach a conclusion. However, a maximum permitted quantity of the residual monomer in the finished material or article, expressed in terms of isocyanate groups (NCO) of 1mg kg^{-1} has been laid down in directive 90/128/EEC (20). No data is available yet for the aliphatic diisocyanate IPDI, and the committee has not expressed any opinion.

Under actual conditions of use material present in the polyurethane adhesives employed in boil in the bag laminates can be altered. Material that was originally non toxic becoming toxic by the changes taking place. Isocyanate based polyurethane adhesives are susceptible to hydrolysis and thermooxidation, and both these chemical reactions can occur during the life span of a normal boil in the bag laminate. One of the main hydrolysis products of residual MDI is 4,4'-methylenedianiline (MDA). This has been found to have cancer inducing activity (245) and is a potent hepatic toxicant (246). The Food and Drugs Administration (FDA) has determined a limit of 0.54μg dm^{-2} for the hydrolysis product MDA (247), but no account is taken of the hydrolysis product by the SCF.

5.2 EXPERIMENTAL

Commercial polyurethane adhesives are mixtures of either aromatic or aliphatic diisocyanates with either an aromatic or aliphatic polyester or polyether. It is therefore necessary to ascertain what is present in these adhesives, and what components have a potential to migrate.

In order to investigate the materials migrating from the adhesive a series of experiments were undertaken to identify the components present in commercial polyurethane adhesives, and to determine the overall migration characteristics of different adhesives. Migration studies conventionally require a thin film of the substrate to optimise the measurements. This approach was considered for polyurethane adhesives since they are solvent based and may therefore be cast, but at the typical loadings used in laminates, around 3-5g m^{-2} the film would be only a few microns thick and not readily amenable to study. An alternative approach was to use a range of adhesives bonding two previously well categorised polyolefin films. Such laminates are not used commercially for food packaging and were prepared specifically for this project.

5.2.1 Materials

Sample Laminates

The five laminates used in this investigation were all obtained from the same commercial source, and the constituents employed in the adhesive were known.

Laminate Samples	Type of Adhesive	
	Polyol	Diisocyanate
50μm HDPE / 15μm LLDPE	Polyether	Aromatic
15μm LLDPE / 50μm HDPE	Polyether	Aromatic
50μm LLDPE / 15μm HDPE	Polyether	Aromatic
50μm LLDPE / 50μm LLDPE	Aromatic Polyester	Aromatic
50μm LLDPE / 50μm LLDPE	Aliphatic Polyester	Aromatic

Adhesive Samples

Three commercial polyurethane adhesives used in the production of commercial laminates were analysed. One adhesive was classified as aromatic and the others aliphatic.

Reagents

The following reagents were used :-

Millipore water - (resistivity 18MΩ cm - milli-RO15 water system)

Napolina olive oil - purchased at retail outlet

HPLC grade methanol, and HPLC grade dichloromethane
(Rathburn, Walkerburn, U.K.)

HCl specific gravity 1.18 35%
4,4'-Methylenebis (phenyl isocyanate) **(4,4'-MDI)**
(BDH Laboratory Supplies, MERCK Ltd, Lutterworth, Leicester, U.K.)

3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate **(IPDI)**
1,6-Diisocyanato-hexane **(HDI)**
(Aldrich Chemical Company, Gillingham, Dorset, U.K.)

Polyester Resin - Holdens Surface Coatings Ltd.

5.2.2 Investigation of overall migration from polyurethane adhesives

The overall migration experiments were based on a sixty minute immersion of the test specimens in boiling 18MΩ millipore water or oil at 100°C. Where the pouch was used the food simulant was at ambient temperature prior to immersion. Conventional total immersion testing single sided cell and pouch tests were all used for comparison (123, 76). Sample sizes ranged from 20 ×10cm for the total immersion tests, to 20 × 20cm for the pouch tests. Pouches were prepared using a Hulme Martin dual electronic sealer.

For overall migration determinations using an aqueous simulant the aqueous extract was slowly evaporated and the residue collected and dried to constant mass. With oil

simulants the mass loss on the test specimens are not so simple to determine and the standard CEN methodology was employed (183,184).

The results for the overall migration from polyurethane adhesives into aqueous and oil simulants using the polyolefin / adhesive / polyolefin film are recorded in Table 5.4. Also tabulated for comparison are the anticipated values for the polyolefin films alone. To prevent repetition of work previously carried out on some of these laminates with oil simulants the data was abstracted from results obtained by Mulroy (123). These results were derived from several different test methods, so it is therefore appropriate to cite only the range of migration results obtained.

Sample Laminate	Overall Migration (mg dm^{-2})			
	Aqueous Simulant		Oil Simulant	
	Laminate	Film Only	Laminate	Film Only
50μm HDPPE / 15μm LLDPE *	< 0.1	< 0.1	7.4 - 10.9	7.5 - 9.7
15μm LLDPE / 50μm HDPE *	< 0.1	< 0.1	7.4 - 10.7	7.5 - 9.7
50μm LLDPE / 15μm HDPE *	0.1	0.1	4.7 - 6.7	4.7 - 6.4
50μm LLDPE / 50μm LLDPE *	0.1	0.1	9.0 - 13.0	8.8 - 12.2

* = side of laminate in contact with food simulant for single sided cell or pouch tests.

Table 5.4 Overall migration data for a range of laminates constructed from a polyurethane adhesive and polyethylene

The results obtained for oil simulants indicate that the total migrants from the laminates were found to be slightly higher than the corresponding film, indicating a contribution from the adhesive layer of the laminate. However, the contribution from the adhesive is minor, and less than 1mg dm^{-2} in most cases. When an aqueous food simulant was employed the levels of species migrating were significantly less due to the ability of the oil to act as a plasticizer and penetrate the polyolefin film. In addition no significant differences were observed in the amount of material migrating from the adhesive when different polyurethane adhesives were used.

5.2.3 Investigation of individual migrants from polyurethane adhesives

Gravimetric measurement is a suitable technique for obtaining overall migration measurement of material migrating from the polyurethane adhesive into aqueous and oil simulants. However, gravimetric analyses are unable to discriminate between the various species migrating from the adhesive. It is also not sensitive enough to monitor individual species such as diisocyanates and diamines, where amounts in the μg dm^{-2} range are known to give cause for concern.

For a long time the common method for the determination of aromatic isocyanates in the environment has been the colorimetric method devised by Marcali (77). This involves the hydrolysis of the isocyanate to the corresponding aromatic amine, which is diazotised and coupled to form a coloured azo compound. Such a colorimetric analysis is not readily extended to aliphatic isocyanates which do not form stable diazonium salts. To overcome this Pilz and Johann (248) developed a colorimetric method in which the amine formed on hydrolysis is reacted with 1-fluoro-2,4-dinitrobenzene. Despite both colorimetric methods being more specific than gravimetric determinations they still lack sensitivity and selectivity, and have now to a great extent been replaced by chromatographic methods.

High performance liquid chromatography (HPLC) has been extensively used, but before the analysis can be undertaken the isocyanates have to undergo derivatisation. Table 5.5 lists the many reported derivatising agents used for this purpose. All of these reagents react with isocyanates to form urethane or urea derivatives for ultraviolet, fluorescence or electrochemical detection. However, the formation of derivatives before chromatography often leads to sample loss and interference from other migrants. Other problems encountered with the use of derivatising agents include oxidation of the reagent, both during and after sampling, and deterioration of the HPLC column by excess use of reagent in samples.

The major limitation of HPLC methods is that they are only suitable for the analysis of free unreacted isocyanates present in either the laminate or the aqueous / oil food simulant. If any of the isocyanates migrating have undergone hydrolysis to the corresponding amine they will not undergo derivatisation.

Reagent	Detection Method	Reference
N-(4-nitrobenzyl)-N-n-propylamine "Nitro reagent"	UV	249 - 255
1-(2-pyridyl)-piperazine	UV	256
1-(2-methoxyphenyl)-piperazine	UV, EC	254, 257 - 260
1-Naphthalemethylamine	F	261
9-(N-methylaminomethyl)-anthracene	F, UV	259, 262
N-methyl-1-naphthalenemethylamine	F, UV	263
p-Aminophenol	EC	264
3-(2-aminoethyl)-indole	F, EC	265

UV = Ultraviolet detection EC = Electrochemical detection F = Fluorescence detection

Table 5.5 HPLC methods for the determination of isocyanates in the environment

Several workers have determined the presence of the corresponding diamines of toluene diisocyanate in aqueous extracts of food contact boil in the bag pouches using HPLC and GC-MS (266-269). However, little work has been reported on the analysis of hydroxyl terminated polyethers, polyesters and other diisocyanates used in polyurethane adhesives which also have the potential to migrate.

In this investigation a HPLC technique with UV detection at 230nm was developed to compare the migrants from different polyurethane adhesives into aqueous food simulants. A GC-MS method was then employed to characterise the species migrating, in addition to examining the diisocyanate components of three commercial polyurethane adhesives.

5.2.3.1 Identification of polyurethane adhesive raw materials and migrants

The sample laminate 20 × 10cm was chopped into 1cm squares and placed in a round bottomed flask with 100cm^3 of 18MΩ millipore water. The laminate was then boiled under reflux for one hour and the aqueous phase removed for analysis.

For HPLC analysis 50cm^3 of the aqueous solution was rotary evaporated down under vacuum in a water bath at a temperature of 70°C to a volume of 4cm^3. The

concentrated solution was then transferred to a $5cm^3$ volumetric flask where it was made up to volume with an 80 : 20 mixture of methanol / water. Each sample was then analysed employing the chromatographic conditions cited in Table 5.6.

The remaining $50cm^3$ of aqueous solution was transferred to a separating funnel where $1.0cm^3$ of 0.2M HCl was added, and the aqueous solution solvent extracted with $2 \times 50cm^3$ aliquots of dichloromethane. The pooled dichloromethane extracts were then reduced to a volume of $1cm^3$ by the use of a Wheaton concentrator, immersed in a water bath at a temperature of 50°C. The concentrated sample was then analysed by GC-MS using the chromatographic condition cited in Table 5.7.

The three commercially used adhesives were also analysed by GC-MS using the conditions cited in Table 5.7. In each case the samples were dissolved in dichloromethane, and where possible the identity confirmed by the addition of isocyanate standards.

Eluent	:	45 : 55 Methanol / Water
Flow rate	:	$1.5cm^3\ min^{-1}$
Pump	:	Pye Unicam PU4015
Injector	:	Marathon Autosampler 100µl sample loop at 30°C
Column	:	Alphasil 5µm ODS C_{18} 250 x 4.6mm i.d. HPLC Technology Ltd. Macclesfield, UK.
Detector	:	ACS Model 750/11/AZ UV at 230nm
Integrator	:	Hewlett Packard HP3394A

Table 5.6 Summary of HPLC experimental conditions for the analysis of migrants from polyurethane adhesives

Instrument

GC	:	Hewlett Packard 5890
MS	:	VG TRIO 3

GC Conditions

Column	:	25m x 0.25mm SE-54 Capillary WCOT quartz fused silica column
Carrier Gas	:	Helium 1cm^3 min^{-1}
Split	:	20 : 1
Oven programme	:	100°C for 1min then ramp to 260°C at 20°C min^{-1} hold for 5 min
Injector temperature	:	250°C

MS Conditions

Mass Range	:	30 - 700
Repeat rate	:	1 scan s^{-1}
Data handling	:	VG/PDP11 system

Table 5.7 Summary of experimental conditions for gas chromatography-mass spectrometry (GC-MS) analysis of polyurethane adhesive raw materials and migrants

The eluent chosen for the HPLC investigation is unsuitable for the analysis of underivatised diisocyanates, since any such species would react with either the water or the alcohol. However, the chromatograms obtained showed distinct differences in the materials migrating from the different types of adhesives. Figure 5.1 compares adhesives containing aromatic and aliphatic polyesters combined with the same aromatic diisocyanate with the analysis of migrants from the polyester resin alone. The chromatograms obtained for the migrants from the two adhesives showed very few similarities. However, comparison of the chromatograms from the adhesive containing the aromatic polyester and the polyester resin alone indicated the presence of several peaks with the same retention times. Inferring that the migrants from the polyester resin and the adhesive containing the aromatic polyester were similar. This was further reinforced by consideration of the constituents of the adhesives and remembering that

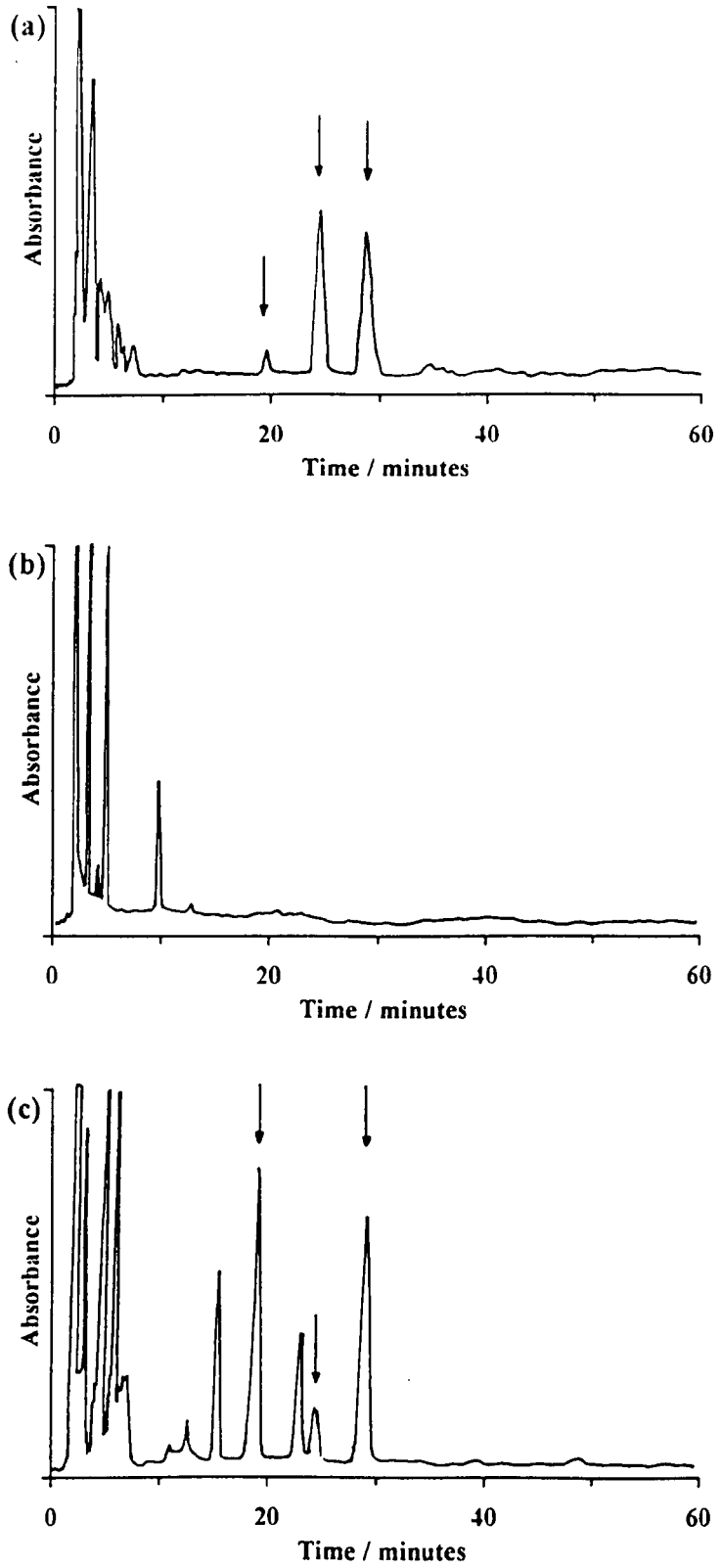


Figure 5.1 **HPLC analyses of migrants from two adhesives containing the same aromatic diisocyanate but different polyol's with an aromatic polyester resin.**

a: Adhesive containing aromatic polyester

b: Adhesive containing aliphatic polyester c: polyester resin

UV detection is being employed. Both materials that produced significant migrants on the chromatogram contained an aromatic substituent in the polyol (isophthalic acid), which is a strong UV absorber, whereas adhesives containing aliphatic constituents in the polyol were not as efficient at absorbing in the UV.

GC-MS analysis of three commercially used polyurethane adhesive samples indicated that the aromatic adhesive contained 4,4'-MDI as expected, but also significant quantities of IPDI and HDI. The two other commercial aliphatic adhesives supplied contained only the anticipated diisocyanates, one being HDI and the other IPDI.

For the laminates constructed from adhesives containing aromatic diisocyanates the migrating compounds which were detected and identified are :-

Ethyl acetate	-	solvent used to disperse the adhesive
Aniline	-	residue from production of 4,4'-MDI
4,4'-MDI	-	Diisocyanate monomer used in production of adhesive

It is unusual to find 4,4'-MDI in aqueous extracts from laminates, since any isocyanate would be expected to be readily hydrolysed to the corresponding diamine. Subsequent investigations by Lawson and Bird (270) have shown that MDI derivatives are unstable under mass spectrometry conditions and invariably produce fragmentation patterns associated with MDI itself.

5.2.3.2 LC-MS analysis of migrants from the adhesives

In the previous Section 5.2.3.1, HPLC investigations of migrants from different types of adhesives into aqueous food simulants indicated a relationship between the nature of the adhesive and the chromatogram obtained. Figure 5.1 indicated that some of the migrants from the aromatic based adhesive have the same retention times as some of the components found in the polyester resin used in its manufacture. Inferring that some of the migrants observed in the HPLC analysis were from the polyol used in the formulation of the adhesive. LC-MS techniques were therefore used to identify these components. Several well known LC-MS interfaces exist e.g. electrospray, thermospray and fast atom bombardment, but all suffer the same limitations, the degree of fragmentation is limited. In general only a large m+1 ion is observed, and there is no suitable general database from which unknown species can be identified. The particle beam interface produces conventional electron impact (EI) mass

spectra for some LC eluents which can then be compared with conventional databases. To date, however, there is little information in the literature concerning results from this type of interface. In order to obtain the maximum amount of information possible, selected extracts from aqueous migration experiments were analysed by both the particle beam and dynamic fast atom bombardment techniques Frit-FAB.

Instrument

MS	JEOL AX - 505WA
HPLC	HP - 1090L

MS Conditions

Acceleration voltage	3KV
Ionization	FAB
Polarity	Positive
Scan range	50 - 1500
Scan speed	5 s

HPLC Conditions

Column	Capcellpak ODS (4.6mm i.d. x 150mm)
Eluent	A = Water : B = Methanol B = 20% at 0 min to B = 70% at 25 min. Linear gradient
Flow	$1cm^3\ min^{-1}$
Column temperature	40°C
UV detector wavelength	230nm
Injector volume	100µl

FAB Conditions

Neutral gas	Xe
Gun potential	4KV
Matrix	3% Glycerol / Methanol ($0.3cm^3\ min^{-1}$ post column addition)

Table 5.8 Experimental conditions for Frit-FAB LC-MS analyses.

Instrument

MS	VG TRIO 1
HPLC	HP - 1090L

MS Conditions

Scan range	30 - 600
Scan speed	5 s

HPLC Conditions

Column	Spherisorb S3 ODS (2mm i.d. x 150mm)
Eluent	A = Water : B = Methanol B = 45% from 0 to 8 min then ramped to B = 100% at 20 min. Linear gradient
Flow	$0.3cm^3\ min^{-1}$
Column temperature	40°C
Injector volume	50µl

Table 5.9 Experimental conditions for particle beam LC-MS analyses.

Two of the three laminates examined contained aromatic isocyanates and aromatic polyester polyols whilst the final laminate contained an aromatic isocyanate and a polyether polyol. Sample laminates of dimensions 20 × 10cm were chopped into 1cm squares and boiled under reflux for one hour in $100cm^3$ of millipore water. The aqueous phase was then rotary evaporated under vacuum at 60°C to approximately $6cm^3$, and made up to a final volume of $10cm^3$ using methanol / water 80:20 solution. These solutions were then analysed by both Frit-FAB and particle beam LC-MS techniques using the instrumental operating parameters cited in Tables 5.8 and 5.9.

Identification of polyol based migrants

The molecular ions observed from the Frit-FAB experiments are shown in Table 5.10. These results show some commonality in the identified species migrating from the two different aromatic adhesive based laminates. The molecular ions cited in Table 5.10 may be rationalized in terms of the polyester resin used in the adhesive. In these film samples the polyester resin was produced by the copolymerization of a mixture of diethylene glycol, adipic acid and isophthalic acid. A range of oligomers can be envisaged, based on different combinations of

these starting materials. Some of these combinations and the appropriate molecular ions are shown in Table 5.11. These combinations account for all but two of the observed, but unidentified, migrants from the aromatic adhesive based laminate samples.

The analysis of the polyurethane adhesive incorporating an aliphatic polyether showed a range of species with molecular weights as follows :- 376, 390, 406 and 498. Attempts to formulate possible structures for these species based on a knowledge of the polyether system has so far been unsuccessful and samples of the resin can not be obtained for comparison. There is some evidence to suggest a similarity with propylene oxide derivatives, but further work is required to identify the species. The data obtained from the LC-MS analysis of this sample is not identical to the HPLC trace since the UV detector employed only responds to compounds with a good chromophore. Aliphatic polyesters and polyethers are poor UV chromophores and do not show up as large peaks on HPLC chromatograms. However, aromatic polyesters are strong UV chromophores and these show up as large peaks on the HPLC chromatograms.

Indicated Molecular Ion	Laminate 1	Laminate 2
450	√	×
216	√	×
470	√	×
490	√	×
432	√	×
452	√	√
472	√	√
648	×	√
668	×	√
688	×	√
708	×	√
697	×	√

× = Species not detected, presumed not to be present since different polyol polymerization mixture incorporated into the adhesive.

Table 5.10 Observed molecular ions from two laminates containing a polyurethane adhesive consisting of aromatic polyesters and aromatic isocyanates

Structure	Calculated Molecular Weight	M^+ Observed Molecular ion
DEG – IPA | | IPA – DEG	472	√
IPA – DEG – IPA – DEG	490	√
DEG – AA | | AA – DEG	432	√
AA – DEG –AA – DEG	450	√
DEG – AA | | IPA – DEG	452	√
AA – DEG – IPA –DEG	470	√
IPA – DEG – AA – DEG	470	√
AA – DEG – AA | | DEG – AA – DEG	648	√
AA – DEG – AA – DEG – AA – DEG	650	×
AA – DEG – IPA | | DEG – AA – DEG	668	√
AA – DEG – IPA | | DEG – IPA – DEG	688	√
IPA – DEG – IPA | | DEG – IPA – DEG	708	√

Note : AA = Adipic Acid DEG = Diethylene glycol IPA = Isophthalic acid

Table 5.11 Possible oligomers from polyester starting materials compared with the observed data

5.3 SUMMARY

This investigation has confirmed the presence of migrants from the adhesives used in boil in the bag laminates into both aqueous and oil food simulants. Overall migration results showed that the total amount migrating from the adhesive was relatively small, not exceeding 1mg dm^{-2} even when an oil simulant was used.

HPLC and LC-MS analysis of these migrants confirmed the presence of aromatic polyesters from the polyol constituent of the adhesive. However, migrants from adhesives containing aliphatic polyesters and polyethers did not give such large peaks on the UV trace as a direct cosequence of their poor UV absorbance. GC-MS analysis was unable to confirm the identity of these polyols due to their lack of volatility. Other migrants that were found included ethyl acetate, aniline and a derivative of 4,4'-MDI.

Analysis of commercial polyurethane adhesives used in the production of boil in the bag laminates also confirmed the complex nature of commercial adhesives. The diisocyanate component of an adhesive that was classified by the supplier as being aromatic was found to also contain significant quantities of aliphatic diisocyanates.

CHAPTER 6 : MIGRATION FROM COMMERCIAL BOIL IN THE BAG FILMS AND POUCHES

6.1 INTRODUCTION

Throughout this research the emphasis of the work has always been towards the study of commercial materials as would be seen in retail outlets and used by the consumer. Such materials are not as well specified as analar grade chemicals and the analytical work has consequently been more complex.

Preliminary work in the previous three chapters on the individual components that make up commercial boil in the bag pouches has allowed some of these problems to be identified e.g. Irgafos 168 in Irgafos PEPQ, and enabled suitable analytical techniques to be developed.

As previously mentioned in Chapter 2 commercial boil in the bag films are usually constructed from a sandwich of polyethylene and nylon 6 films, bonded with a polyurethane based adhesive, but coextruded materials are now becoming increasingly more common. In a typical commercial boil in the bag the polyolefin layer is on the inside, with the added advantage of being a heat sealable material, for rapid closure after filling. The outer layer of polyamide provides the pack with both its physical strength and non permeability requirements. Typical total film thickness for commercial boil in the bag films range from 50 - 150μm.

For boil in the bag laminates demands are made on the water resistance of the adhesive, and it has to resist the stresses induced by the deep drawing of the laminate and differential expansion of the laminate films on heating. Consequently a highly cross linked two component polyurethane adhesive is employed. A typical laminate sheet is produced by coating the adhesive formulation , diluted in either ethyl acetate or methyl ketone, onto one of the films using a roller. The solvent is allowed to evaporate off and the two films are passed between a heated nip roller to complete the lamination. The amount of adhesive applied varies between 2 - 8gm^{-2} depending on the type and application of the laminate.

As can be seen in Section 5.1 a laminate constructed from a polyurethane adhesive is an extremely complex material. By contrast the production of a comparable film by coextrusion techniques does appear to offer a far simpler material, in terms of the number and

nature of the components utilized. In coextrusion, two or more thermoplastic resin melts are extruded simultaneously from the same die. For coextruded films composed of polyamide and polyolefin the polymer adhesion is poor. To overcome this problem the plastic materials are bonded with a thermoplastic adhesive layer commonly known as a tie layer. For nylon / polyethylene films the tie layer can be made from either ethylene vinyl alcohol (271) or ethylene vinyl acetate (272). Initial films produced by this method did not match the peel strength of the polyurethane bonded laminates, particularly in boiling water, but this problem has now been overcome and laminates able to withstand cooking conditions for boil in the bag meals have now been developed (273).

6.2 EXPERIMENTAL

The migrants from the laminates and coextruded films have been examined by conventional gravimetric methods, gas and liquid chromatography techniques and an improved version of the Marcali (77) method for diisocyanates and diamines. The volatile components in the migrants have been analysed by GC-MS methods and the remaining fraction of larger involatile species by HPLC and LC-MS techniques.

Migration studies have been carried out with the films in two formats. Initially work utilized the total immersion approach with the films chopped into 1 × 1cm pieces, an approach adopted to facilitate in the migration and subsequent identification of species migrating. Realistic migration data was then obtained using the boil in the bag materials in the pouch format, where possible using commercially prepared pouches.

6.2.1 Materials

Sample Films

All the boil in the bag films investigated were of commercial quality, and more importantly they were laminated or coextruded on professional machines to give an adhesive or tie layer of dimensions normally acceptable to the food packaging industry. A total of 38 films used in the production of commercial boil in the bag films were investigated. DRG, Bristol and Holdens Surface Coatings, Birmingham have supplied either known materials direct from production runs or have specially laminated materials of different but commercial grade adhesive systems. Finally samples of laminates and coextruded films in both the sheet and preformed pouch format have been supplied by several food retailing organizations.

Reagents

The following reagents were used:

Millipore water - (resistivity 18MΩ cm -milli-RO15 water system)

Napolina olive oil - purchased at retail outlet

HPLC grade acetonitrile, HPLC grade methanol and
HPLC grade dichloromethane
(Rathburn, Walkerburn, U.K.)

Concentrated hydrochloric acid
Glacial acetic acid
Sodium nitrite
Sulphamic acid
(Fisons, Loughborough, Leicestershire, U.K.)

Dow Corning 200/50 cs Silicone fluid
4,4'-methylene dianiline **(MDA)**
Sodium bromide
N-(1-naphthyl) ethylene diamine dihydrochloride **(NEDD)**
(Merck / BDH, Lutterworth, Leicestershire, U.K.)

Polyester Resin - (Holdens Surface Coating LTD. Birmingham, U.K.)

The commercial antioxidants Irganox 1010, Irganox 1076, Irganox 1330 (1,3,5-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)-2,4,6-trimethylbenzene), Irgafos 168 and Irgafos P-EPQ were supplied by Ciba-Geigy Additives, Hulley road, Macclesfield, Cheshire, U.K.

ε-Caprolactam 99+% [Gold label]

3,5-di-tert-butylphenol **(3,5-DTBP)**

2,4-di-tert-butylphenol **(2,4-DTBP)**

2,6-di-tert-butylphenol **(2,6-DTBP)**

2,6-di-tert-butyl-1,4-benzoquinone **(2,6-DTBBQ)**

2,6-di-tert-butyl-4-methylphenol **(BHT)**

2,4,6-tri-tert-butylphenol **(2,4,6-TTBP)**

(Aldrich Chemical Company, Gillingham, Dorset, U.K.)

Specific solutions for modified Marcali method :

Sodium nitrite solution :- 3 and 5g of sodium nitrite and sodium bromide respectively in $100cm^3$ of millipore water.

Sulphamic acid solution :- 10g of sulphamic acid in $100cm^3$ of millipore water.

N-(1-naphthyl) ethylene diamine dihydrochloride solution (NEDD) :- 600mg of NEDD was dissolved and made up to volume in a $25cm^3$ volumetric flask with millipore water.

Acid medium :- $35cm^3$ of conc. HCl and $22cm^3$ of glacial acetic acid in $1000cm^3$ of millipore water.

1.2N HCl :- $51.5cm^3$ of conc. HCl (36%) in $500cm^3$ of millipore water.

0.6N acetic acid :- $17cm^3$ of glacial acetic acid in $500cm^3$ of millipore water.

MDA Calibration solution :- 25mg of 4,4'-methylene dianiline (MDA) in $500cm^3$ of 1% HCl solution. $5cm^3$ of this solution was diluted to $500cm^3$ with a 1% acetic acid solution, to give a solution containing $0.5\mu g\ cm^{-3}$ MDA.

6.2.2 Overall migration data

The overall migration experiments were based on a 60 minute immersion of the test specimens in 18MΩ millipore water, or oil at 100°C. Where the pouch was used the food simulant was at ambient temperature prior to immersion. Conventional total immersion tests, single sided cell and pouch tests were used as convenient, and for comparison purposes (123,76). Sample sizes ranged from 20 x 10cm for the total immersion tests, to 20 x 20cm for the pouch tests. Pouches were prepared using a Hulme Martin dual electronic sealer where commercial samples were not available.

For overall migration determinations using an aqueous simulant the millipore water was slowly evaporated and the residue collected and dried to constant mass. With oil simulants the mass loss on the test specimens are not so simple to determine and the standard CEN methodology was employed (183,184).

The results obtained for the overall migration from laminates and coextruded films into aqueous and oil simulants are recorded in Table 6.1. To prevent repetition of work previously carried out on some of the laminates with oil simulants, the data was abstracted from results compiled by Mulroy (123).

In all cases the results cited in Table 6.1 are based on replicate analyses of similar film samples obtained from a variety of commercial sources. It is therefore more appropriate to cite the range of values obtained for the overall migration data. As can be seen these migration values are generally below the specified maximum of 10mg dm^{-2}. Migration levels into the aqueous food simulant from films in the pouch format were found to be lower than those for oil simulants, due to the ability of the oil to penetrate into the polyolefin and act as a plasticizer. The anomalously high value observed for the 50μm NY6 / 50μm LLDPE laminate in an oil simulant resulted from high levels of calcium stearate incorporated into the film (123). As expected a larger amount of material was found to migrate from chopped films into an aqueous food simulant than pouches. The majority of the material migrating from the films into the aqueous food simulant can probably be attributed to caprolactam and oligomers of the nylon (Chapter 4). Therefore, these oligomers of nylon can migrate into the aqueous food simulant when the film is chopped. However, in the pouch format these oligomers would have to migrate through the adhesive and polyolefin layers before entering the aqueous food simulant. In addition, no significant differences were noted in the overall amount of material migrating from similar laminates constructed from aliphatic or aromatic based adhesives into aqueous food simulants.

Sample	Overall migration / mg dm^{-2} Chopped	Pouches
Aqueous Food Simulant		
Laminate (Aromatic Adhesive)		
20μm NY66 / 50μm LLDPE *	1.1 - 1.3	0.1 - 0.2
70μm NY6 / 75μm LLDPE *	4.8 - 5.6	0.8 - 1.2
50μm NY6 / 50μm LLDPE *	2.0 - 4.4	1.0 - 1.5
15μm NY6 / 50μm LLDPE *	2.2 - 3.3	0.2 - 0.8
Laminate (Aliphatic Adhesive)		
20μm NY66 / 50μm LLDPE *	1.1 -1.3	0.0 - 0.1
70μm NY6 / 75μm LLDPE *	4.6 - 5.3	0.6 - 1.2
50μm NY6 / 50μm LLDPE *	2.7 - 3.9	0.9 - 1.3
15μm NY6 / 50μm LLDPE *	2.0 - 3.0	0.2 - 0.6
Coextruded Film		
30μm NY6 / 40μm LLDPE *	1.5 - 1.7	0.0 - 0.1
70μm NY6 / 70μm LLDPE *	3.0 - 3.6	0.1 - 0.3
Oil Simulant		
Laminate (Aromatic Adhesive)		
50μm NY6 / 50μm LLDPE *	4.3 - 7.0	4.1 - 6.5
15μm NY6 / 50μm LLDPE *	+	7.0 - 37.9

* = Side in contact with food simulant for single sided pouch tests.
NY6 = Nylon 6
NY66 = Nylon 6,6
LLDPE = Linear Low Density Polyethylene
\+ = No data available

Table 6.1 Overall migration data for a range of laminates and coextruded films

6.2.3 GC-MS analysis of migrants

Gravimetric measurement whilst being a suitable technique for obtaining an overall migration value for the total amount of material migrating from boil in the bag films into aqueous and oil food simulants, is unable to identify and quantify the species migrating. In order to do this the food simulant after the migration period must be subjected to either chromatographic or spectroscopic analysis, or both to identify and hence quantify the species present.

GC-MS analyses were initially used to identify the specific volatile components migrating from the commercial boil in the bag films. To facilitate in the identification of migrants from commercial boil in the bag films, samples of 20 × 10cm area were chopped into 1cm squares and placed in a round bottomed flask with 100cm^3 of aqueous or oil food simulant. The chopped film and the simulant were then heated for one hour at 100°C prior to removal for analysis

On cooling the solution was decanted off from the residual film, and 1.0cm^3 of 0.2M HCl was added. The simulant was then extracted with two 100cm^3 aliquots of dichloromethane. The food simulant layer was then made basic by the addition of 1.5cm^3 of 0.2M NaOH, and the simulant again extracted with a further two 100cm^3 aliquots of dichloromethane. These dichloromethane extracts were then pooled and reduced to a volume of 1cm^3 by the use of a Wheaton concentrator, immersed in a water bath at a temperature of 50°C. The concentrated samples, plus a blank prepared through the same procedure as outlined above were then analysed by GC-MS using the chromatographic conditions cited in Table 6.2.

Instrument		
GC	:	Hewlett Packard 5890
MS	:	VG TRIO 3
GC Conditions		
Column	:	25m x 0.25mm SE-54 Capillary WCOT quartz fused silica column
Carrier Gas	:	Helium 1cm^3 min^{-1}
Split	:	10 : 1
Oven programme	:	35°C for 2min then ramp to 65°C at 15°C min^{-1} then ramp to 250°C at 20°C min^{-1} hold for 10 min
Injector temperature	:	250°C
MS Conditions		
Mass Range	:	30 - 700
Repeat rate	:	1 scan s^{-1}
Data handling	:	VG/PDP11 system

Table 6.2 Summary of experimental conditions for GC-MS analysis of migrants from boil in the bag films.

The migrants identified showed some variations for different films (Table 6.3) which resulted from the different materials used in the films and possibly also the age of the films. In some instances it is understood that films are retained by the manufacture for a set period prior to use, to allow the film to condition. It is assumed that this conditioning includes the loss of residual solvents and other volatile chemicals by evaporation, or to allow completion of 'cure' of the adhesive.

The aliphatic diisocyanate based adhesives and coextruded films have not been studied as extensively as the others, and therefore there is less information available about the relevant migrants. Within the MDI based systems the differences in chemical species observed may be related to levels of impurities in the original adhesive (MDI is derived from aniline) or to degradation factors during use. To date there is no evidence to suggest which is the correct assumption.

Compound	Aromatic Laminate 1	Aromatic Laminate 2	Aliphatic Laminate	Coextruded Film
Phenol		√		
Aniline	√			
Caprolactam monomer	√	√	√	√
BHT	√	√	√	
4-(dimethylamino) benzaldehyde	√			
Diphenylamine	√			
Tributyl phospate	√	√	√	
4-benzylaniline	√	√		
MDI		√		
Antioxidant residue	√	√	√	√
TDTBPP	√	√	√	√
Caprolactam dimer	√	√	√	√

BHT = 2,6-di-tert-butyl-4-methylphenol
TDTBPP = tris-(2,4-di-tert-butyl-phenyl)phosphate

Table 6.3 **Compounds identified by GC-MS to be present in both the aqueous and oil extracts of different films.**

6.2.4 Marcali colourimetric determination of aromatic amines

The identification of several aromatic amines in the aqueous migrants (see Table 6.3), combined with the knowledge that the Marcali test was used by manufacturers as part of a film assessment procedure prompted an investigation of the methodology involved (77).

The migration of aromatic amines from commercial boil in the bag films into an aqueous food simulant was investigated using both chopped and pouch film samples. A variety of different commercial films consisting of various types and thickness of polyethylene and nylon bonded together were studied.

Diazotization-coupling procedure and calibration

A range of standards were prepared containing 0 to 5μg of MDA calibration solution in a 50cm^3 volumetric flask. To each flask was added 10cm^3 of 1.2N HCl and a quantity of acetic acid as outlined below :-

	Blank	**0.5μg**	**1.0μg**	**2.0μg**	**3.0μg**	**4.0μg**	**5.0μg**
0.6N acetic acid /cm^3	20	19	18	16	14	12	10
MDA calibration soln./cm^3	0	1	2	4	6	8	10

To each flask was added 2cm^3 of acetone, followed by 1cm^3 of sodium nitrite solution. The solutions were mixed well and allowed to stand for 3 minutes or until diazotization was complete. Excess nitrite reagent was destroyed with 2cm^3 of sulphamic acid solution. The solutions were shaken until gas evolution was complete (approximately 5 minutes). Finally 2cm^3 of NEDD was added to each flask, the solution mixed well, and then diluted to the mark with purified water.

These solutions were then left to stand for 30 minutes to allow the colour to develop. The optical density of each solution was then measured using the following instrumental parameters, employing purified water in the reference beam.

INSTRUMENT :- Pye Unicam SP6 500 UV/VIS Spectrophotometer

CELL :- 40mm path length [Quartz]

WAVELENGTH :- 560nm

The resulting calibration graph (Figure 6.1) obtained by plotting absorbance against mass of MDA indicated a linear response over the range analysed with a limit of detection of 0.25μg in cell or 0.1μg dm^{-2}.

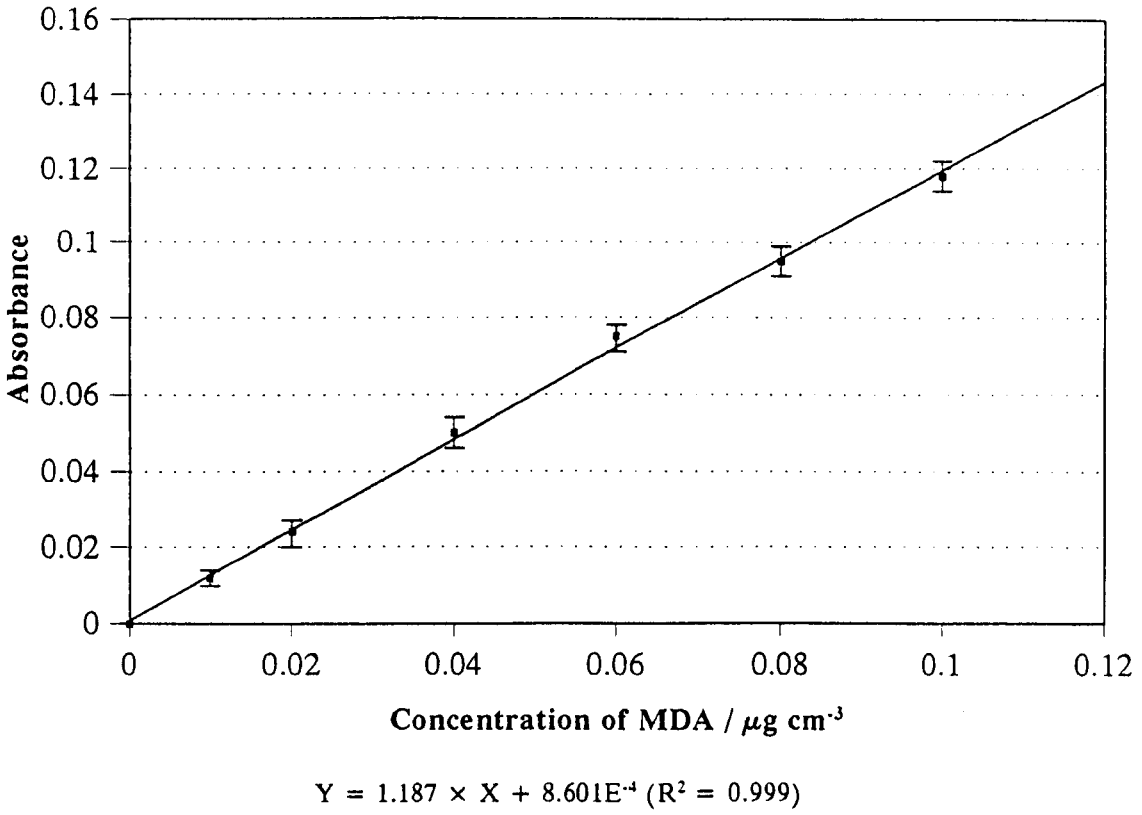


Figure 6.1 Calibration graph for MDA

Chopped and pouch film sample preparation

A variety of different commercial boil in the bag films were investigated. For each sample four pouches of dimensions 11 × 21cm were prepared and heat sealed with a Hulme Martin sealer to give an internal surface area of 4dm^2. Each pouch was then filled with 200cm^3 of millipore water and boiled for 1 hour at 100°C. Where possible commercially prepared pouches of known internal surface area were used. To enable these commercial pouches to be filled with water a small corner was cut off each pouch and the water added prior to resealing the corner. In addition to the four pouch samples, four film samples of dimensions 20 × 10cm were chopped into 1cm squares and placed in a round bottomed flask with 100cm^3 of millipore water. The contents of the flask were then boiled under reflux for one hour.

After boiling, the aqueous contents from each of the chopped and pouch samples

were transferred to clean round bottomed flasks and 1.0cm^3 of conc. HCl was added. The volumes of the solutions were reduced to 20cm^3 using a rotary evaporator under vacuum at a water bath temperature of 60°C. The concentrates were then transferred to 50cm^3 volumetric flasks and the contents of the round bottomed flask washed out with 2 × 10cm^3 aliquots of acid medium, which were then combined with the concentrates. The samples were then subjected to the diazotization-coupling procedure as outlined previously.

A blank was prepared as a reference for both the chopped and pouch films employing the same preparation procedure as outlined above with the exception that no film came into contact with the aqueous food simulant. The recovery of the method was also determined by taking quantities of the MDA solution and diluting to 200cm^3. 1.0cm^3 of conc. HCl was added to each solution these were rotary evaporated down to a final volume of 20cm^3 prior to undergoing the diazotization-coupling procedure.

Using the calibration graph previously obtained (Figure 6.1), the total amount of aromatic amines migrating from the films into an aqueous food simulant were calculated :-

$$\text{Concentration of aromatic amines } (\mu g\ dm^{-2}) = \frac{Ab_{SPL} \times 50}{0.94 \times Cal \times A_{FILM}}$$

Where :-

Ab_{SPL} = UV absorbance value of sample

Cal = Gradient of MDA calibration graph in absorbance units cm^3 μg^{-1}

A_{FILM} = Area (dm^2) of film in contact with food simulant.
This value is 2 for chopped and 4 for pouch films.

NOTE:- Recovery of MDA by rotary evaporation = 94%

The results for the estimated amine migration from both chopped and pouch commercial boil in the bag films are recorded in Table 6.4.

From the data obtained it can be seen that no aromatic amines were found to migrate from either chopped or pouch films into an aqueous food simulant when a commercial coextruded film or laminate constructed using an aliphatic adhesive were used. These results are as expected since an amine based adhesive is not employed in coextruded films and aliphatic adhesives containing aliphatic isocyanates do not produce a coloured complex on diazotization. However, aromatic amines were found to migrate from laminates into aqueous

food simulants when aromatic adhesives were employed in the construction of the laminate. Levels of amine present in aqueous extracts from chopped laminates containing aromatic adhesives indicated levels ranging from 1.1 - 0.6μg dm^{-2}. However, this level was considerably lower when the aqueous simulant from inside the pouch made from the same laminate was analysed. The larger levels of aromatic amine found to be migrating from chopped laminates into aqueous food simulants can be attributed to the glue line of the laminate being in direct contact with the aqueous simulant being analysed. This is not the case when the aqueous simulant from inside a pouch is analysed, since any potential migrants from the adhesive layer would have to penetrate the polyolefin layer before entering the simulant. Therefore, the potential for migration is greater in the chopped rather than the pouch format.

Sample	Migration / μg dm^{-2}	
	Chopped Film	Pouches
Laminate (Aromatic Adhesive)		
100μm NY / 75μm LLDPE *	0.6 ± 0.2	0.1 ± 0.1
70μm NY / 75μm LLDPE *	1.1 ± 0.2	0.1 ± 0.1
50μm NY / 50μm LLDPE *	1.1 ± 0.2	0.1 ± 0.1
15μm NY / 50μm LLDPE *	0.6 ± 0.1	0.1 ± 0.1
RETAIL	0.7 ± 0.2	0.1 ± 0.1
Laminate (Aliphatic Adhesive)		
70μm NY / 75μm LLDPE *	ND	ND
50μm NY / 50μm LLDPE *	ND	ND
15μm NY / 50μm LLDPE *	ND	ND
Coextruded Film		
30μm NY / 40μm LLDPE *	ND	ND
70μm NY / 70μm LLDPE *	ND	ND
20μm NY / 50μm LLDPE *	ND	ND
50μm NY / 50μm LLDPE *	ND	ND

* = Side in contact with food simulant for single sided pouch tests.
NY = Nylon 6
LLDPE = Linear Low Density Polyethylene
ND = Not detected

Table 6.4 Estimated amine migration from boil in the bag chopped films and pouches into an aqueous food simulant.

Despite having a detection limit of 0.1μg dm^{-2} this detection method could not identify the specific chemical species present. The modified Marcali method only allows for the determination of an overall migration level for all aromatic amines present in the aqueous extract. Therefore, the data presented in Table 6.4 is actually a combination of contributions from all of the aromatic amines present in the laminate, for example aniline, diphenylamine, MDA, etc. Within this spectroscopic technique there is no mechanism for determining the contribution from each of the individual aromatic amines migrating. In order to identify and quantify the species migrating from commercial coextruded and laminated films, the food simulant after the migration period must be subjected to chromatographic analysis.

6.2.5 HPLC analysis of antioxidants and degradation products

In Chapter 3 HPLC methodology was developed to analyse antioxidants and their degradation products migrating from polyolefin samples into aqueous and oil food simulants. This same methodology was therefore employed to determine the levels of antioxidants and their breakdown products migrating from boil in the bag films in both chopped and pouch formats.

Sample preparation for aqueous food simulant

For each sample four pouches of dimensions 11 × 21cm were prepared and heat sealed with a Hulme Martin sealer to give an internal surface area of $4dm^2$. Each pouch was then filled with $200cm^3$ of purified water and boiled in the sealed bag for one hour at 100°C. In addition to the four pouch samples, four film samples of dimensions 20 × 10cm were chopped into 1cm squares and placed in a round bottomed flask with $100cm^3$ of purified water. The contents of the flask were again boiled under reflux for one hour at 100°C.

The aqueous food simulants were then rotary evaporated to dryness under an atmosphere of nitrogen, and the residue was redissolved in $10cm^3$ of acetonitrile prior to HPLC analysis for non polar and polar analytes (Table 6.5). Levels of non polar and polar analytes migrating were determined by employing external calibration methods.

Sample preparation for oil simulant

The sample preparation procedure was identical to that for aqueous food simulants with the exception that only $50cm^3$ of silicone oil was used in both the chopped and pouch films. The

silicone oil samples were then extracted using two 25cm^3 aliquots of acetonitrile, in accordance with previously determined recovery data for spiked oil samples (Section 7.3). The combined extracts were then analysed by HPLC as detailed in Table 6.5, employing Irganox 1330 as an internal standard for non polar analyte determinations and 2,4,6-TTBP for polar analytes.

Eluent	:	*Polar analytes* :- 80 : 20 Acetonitrile / Water *Non polar analytes* :- 100% Acetonitrile
Flow rate	:	1.5cm^3 min^{-1}
Pump	:	Pye Unicam PU4015
Injector	:	Marathon Autosampler 100µl sample loop at 30°C
Column	:	Alphasil 5µm ODS C_{18} 250 x 4.6mm i.d. HPLC Technology Ltd. Macclesfield, UK.
Detector	:	ACS Model 750/11/AZ UV at 230nm
Integrator	:	Hewlett Packard HP3394A

Table 6.5 Summary of HPLC experimental conditions for the analysis of antioxidants and their degradation products from boil in the bag films.

The results obtained for a series of different commercially available boil in the bag films are summarised in Tables 6.6 and 6.7. As can be seen the study shows that high molecular weight antioxidants such as Irganox 1010, Irganox 1076, and Irgafos 168 migrate from the film into silicone oil. In addition quantities of antioxidant degradation products were also found to migrate from the 15µm NY6 / 50µm LLDPE laminate constructed from an aromatic based adhesive. At comparable temperatures and times, the levels of antioxidant degradation products were found to be slightly lower for chopped films than pouch films and there are two possible explanations for this occurrence. Firstly it could be a result of the oil simulant not being in contact with all the surfaces of the laminate in the chopped sample. Since a lot of the laminate was protected from exposure to the oil by the surrounding mass of chopped film, which unlike an aqueous simulant does not get agitated at 100°C. However, in the pouch format the oil simulant was in direct contact with all of the polyolefin surface,

	Compound	Migration / μg dm^{-2} Chopped	Pouches
Polar Analytes	3,5-DTBP	80 ± 5	170 ± 10
	2,4-DTBP	8 ± 1	9 ± 2
	BHT	3 ± 0.5	3 ± 0.5
Non polar Analytes	Irganox 1010	40 ± 4	65 ± 5
	Irganox 1076	23 ± 2	30 ± 2
	TDTBPP	110 ± 10	120 ± 10
	Irgafos 168	105 ± 6	152 ± 6

Table 6.6 **Levels of antioxidants and antioxidant degradation products migrating into silicone oil from an aromatic adhesive based laminate (15μm NY6 / 50μm LLDPE)**

Sample	Migration / μg dm^{-2} Chopped	Pouches
Laminate (Aromatic Adhesive)		
20μm NY66 / 50μm LLDPE *	0.7 ± 0.2	0.6 ± 0.2
70μm NY6 / 75μm LLDPE *	0.1 ± 0.1	ND
50μm NY6 / 50μm LLDPE *	ND	ND
15μm NY6 / 50μm LLDPE *	3.0 ± 0.3	2.7 ± 0.3
Laminate (Aliphatic Adhesive)		
70μm NY6 / 75μm LLDPE *	0.2 ± 0.1	0.1 ± 0.1
15μm NY6 / 50μm LLDPE *	0.7 ± 0.2	0.6 ± 0.2
Coextruded Film		
20μm NY6 / 50μm LLDPE *	1.0 ± 0.3	0.8 ± 0.2
50μm NY6 / 50μm LLDPE *	0.7 ± 0.2	0.6 ± 0.2

* = Side in contact with food simulant for single sided pouch tests.
NY6 = Nylon 6
NY66 = Nylon 6,6
LLDPE = Linear Low Density Polyethylene
ND = Not detected

Table 6.7 **Levels of Irganox 1010 migrating from boil in the bag chopped films and pouches into an aqueous food simulant.**

which may account for the slightly higher results. Secondly on making the film into a pouch it was heat sealed , therefore, extra degradation products would be expected as a result of the polymer being heated.

It was also found that much less migration occurred when an aqueous food simulant was used. As can be seen in Table 6.7 the levels of antioxidants migrating into an aqueous food simulant from the films are extremely low and the only compound detected was the antioxidant Irganox 1010. In addition no significant difference in the amount of Irganox 1010 migrating from films in either the chopped or pouch format was observed.

6.2.6 HPLC analysis of caprolactam and oligomers migrating from pouch samples

Data previously obtained in Chapter 4 indicated the presence of significant quantities of the monomer ε-caprolactam, and its oligomers migrating from chopped nylon 6 samples into aqueous food simulants. In this investigation the amount of ε-caprolactam and its oligomers migrating from a series of pouch laminates and coextruded films was determined. The aqueous food simulant both inside and outside the pouch was monitored.

Sample preparation

For each film sample a pouch of dimensions 11 × 21cm was prepared and heat sealed with a Hulme Martin sealer to give an internal surface area of $4dm^2$. Each pouch was then filled with $200cm^3$ of millipore water prior to sealing the pouch with the heat sealer. The pouch was then placed in a 2 litre beaker containing 1.5 litres of boiling 18MΩ water for one hour. After this period the water was removed from the pouch using a syringe. The solution was then rotary evaporated under vacuum at 70°C to a volume of approximately $3cm^3$. This solution was then made up to a final volume of $5cm^3$ using acetonitrile / water 90 : 10 prior to chromatographic analysis.

The remaining 18MΩ water employed as the heating medium was also rotary evaporated under vacuum at 70°C to a final volume of approximately $6cm^3$. This solution was then transferred to a $10cm^3$ volumetric flask and made up to volume with acetonitrile / water 90 : 10. Both of these concentrated samples were then analysed by HPLC employing normal and reverse phase conditions (see Table 6.8).

The caprolactam and oligomer levels in the films were determined employing an external standard of ε-caprolactam and calibration data published by Sedgwick (see Section 4.2.3.2). The resulting data is compiled in Table 6.9.

		Normal phase	**Reverse phase**
Eluent	:	Acetonitrile : Water 82 : 18	Methanol : Water 45 : 55
Flow rate	:	$1.5cm^3\ min^{-1}$	$1.5cm^3\ min^{-1}$
Pump	:	Pye Unicam PU4015	Pye Unicam PU4015
Injector:		Marathon Autosampler 100µl sample loop at ambient temperature	Marathon Autosampler 100µl sample loop at ambient temperature
Column	:	Partisil 5µm silica 250 x 4.6mm i.d. Whatman International Ltd. Maidstone, UK.	Alphasil 5µm ODS C_{18} 250 x 4.6mm i.d. HPLC Technology Ltd. Macclesfield, UK.
Detector	:	Pye Unicam PU4025 UV at 220nm	ACS Model 750/11/AZ UV at 230nm
Integrator	:	Pye Unicam PU4810	Hewlett Packard HP3394A

Table 6.8 Summary of HPLC experimental conditions for boil in the bag films.

The anticipated differences in the migration levels into the food and into the surrounding boiling water are clearly demonstrated. The migration into the surrounding water is clearly important if this water is to be used to heat a vegetable portion of the meal.

Analysis of the migrants from nylon 6 films using the reverse phase conditions, produced a chromatogram with components of identical retention times to those found migrating from the laminates and coextruded film samples. Indicating that the majority of the components observed at short retention times originated from the nylon film. In addition the presence of other migrants at intensities comparable to the ε-caprolactam oligomers were also observed at retention times of between 15 and 35 minutes (see Figure 6.2).

Sample		Migration / mg dm^{-2} ε-caprolactam	Oligomers
Migration into food simulant i.e. through adhesive and polythene	*Laminate (Aromatic Adhesive)*		
	70μm NY6 / 75μm LLDPE	0.05	ND
	15μm NY6 / 50μm LLDPE	0.01	ND
	Laminate (Aliphatic Adhesive)		
	50μm NY6 / 50μm LLDPE	0.08	ND
	15μm NY6 / 50μm LLDPE	0.01	ND
	Coextruded Film		
	30μm NY6 / 40μm LLDPE	0.02	ND
	70μm NY6 / 70μm LLDPE	0.06	ND
Migration into boiling water	*Laminate (Aromatic Adhesive)*		
	70μm NY6 / 75μm LLDPE	1.1	3.8
	15μm NY6 / 50μm LLDPE	0.1	1.3
	Laminate (Aliphatic Adhesive)		
	50μm NY6 / 50μm LLDPE	0.9	2.9
	15μm NY6 / 50μm LLDPE	0.1	1.5
	Coextruded Film		
	30μm NY6 / 40μm LLDPE	0.7	2.5
	70μm NY6 / 70μm LLDPE	1.6	4.4

Results are subject to ± 10% variation

NY6 = Nylon 6
LLDPE = Linear Low Density Polyethylene
ND = Not detected

Table 6.9 Determination of amount of ε-caprolactam and oligomers in heating water and aqueous food simulant.

6.2.7 LC-MS Analyses of migrants from commercial boil in the bag films

HPLC investigations of migrants from boil in the bag laminates into aqueous food simulants have revealed the presence of species which cannot be explained as monomers, oligomers or antioxidants of the specified polymer films. The majority of the peaks up to a retention time of

16 minutes have already been identified as oligomers of nylon 6, but the remainder of the peaks are possibly components derived from the polyol part of the polyurethane adhesive. Comparisons with data obtained in Section 5.2.3.1 indicate comparable retention times between the components found in a polyester resin and some of the migrants from the aromatic based adhesive laminates. In order to identify these unknown compounds both particle beam and dynamic fast atom bombardment LC-MS techniques (Frit-FAB) were employed.

The laminates were chopped up and analysed as detailed in Section 5.2.3.2. Two of the laminates analysed were from different commercial sources but were constructed from 15μm NY6 / 50μm LLDPE ,however, each were known to contain aromatic isocyanates and aromatic polyester polyols. The final laminate had a construction of 50μm NY6 / 50μm LLDPE and was known to contain an aromatic isocyanate and a polyether based polyol.

The subsequent data obtained from the Frit FAB analyses is displayed in Figures 6.3 to 6.5 and confirms the presence of caprolactam and its oligomers up to the nonamer in all the laminate samples analysed. The remainder of the molecular ions observed from the Frit FAB experiments show some commonality in the identified species from the two aromatic polyester polyol based adhesives. Utilizing the data previously obtained in Section 5.2.3.2 it was possible to assign the majority of these compounds to various oligomers produced by the copolymerisation of the starting materials used in polyester resins, i.e. diethylene glycol, adipic acid, and isopthalic acid.

Analysis of the laminate containing a polyurethane adhesive incorporating an aliphatic polyether showed a range of molecular weights but attempts to assign these to possible structures of polyether based systems were unsuccessful and samples of the resin cannot be obtained. However, it is interesting to note that the LC-MS trace is totally different to the HPLC chromatogram obtained (see Figure 6.6), this is a result of the UV detector employed on the HPLC only responding to compounds with good chromophores.

LC-MS analyses with the particle beam interface also confirmed the presence of ε-caprolactam and its dimer in the aqueous food simulant, but despite having good mass spectral data no other oligomers were identified. However, free residual MDI was found in the aqueous extract, Figure 6.7. This is surprising since the extraction procedure and eluent used for the analysis should react with any free residual isocyanate.

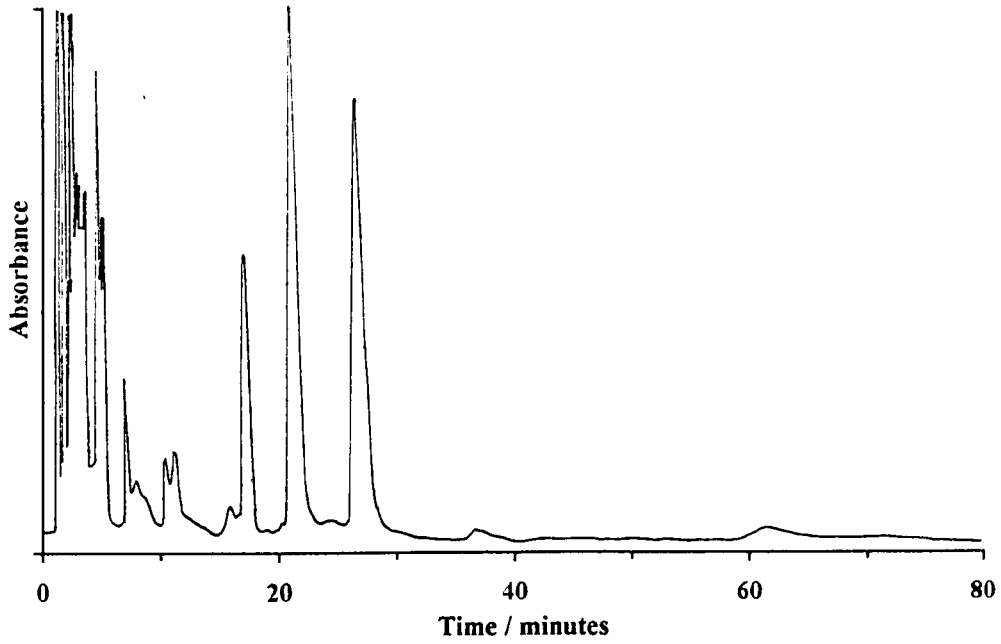
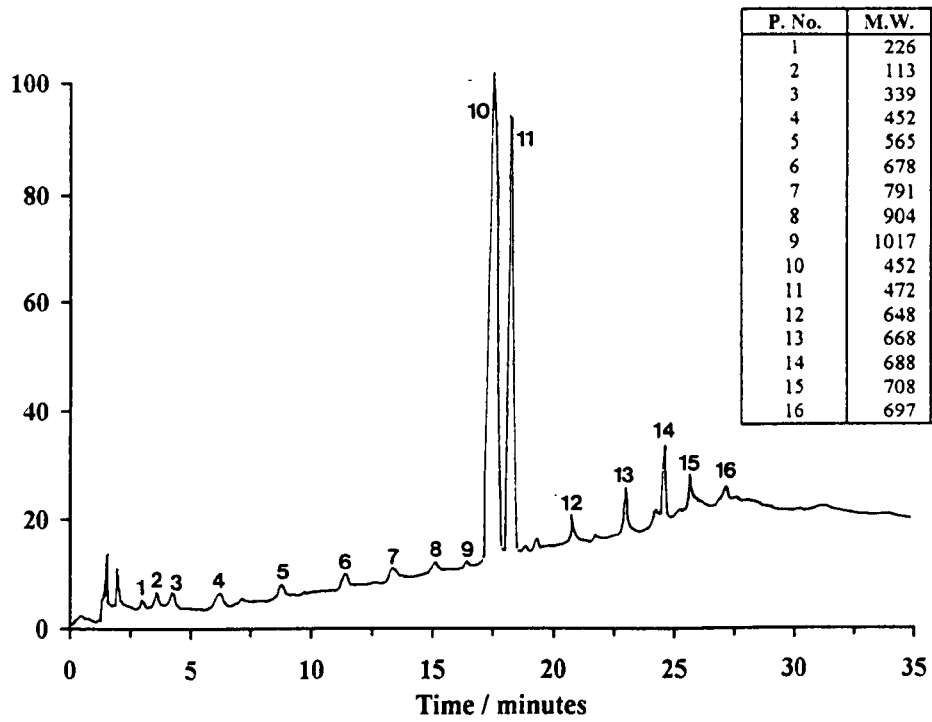
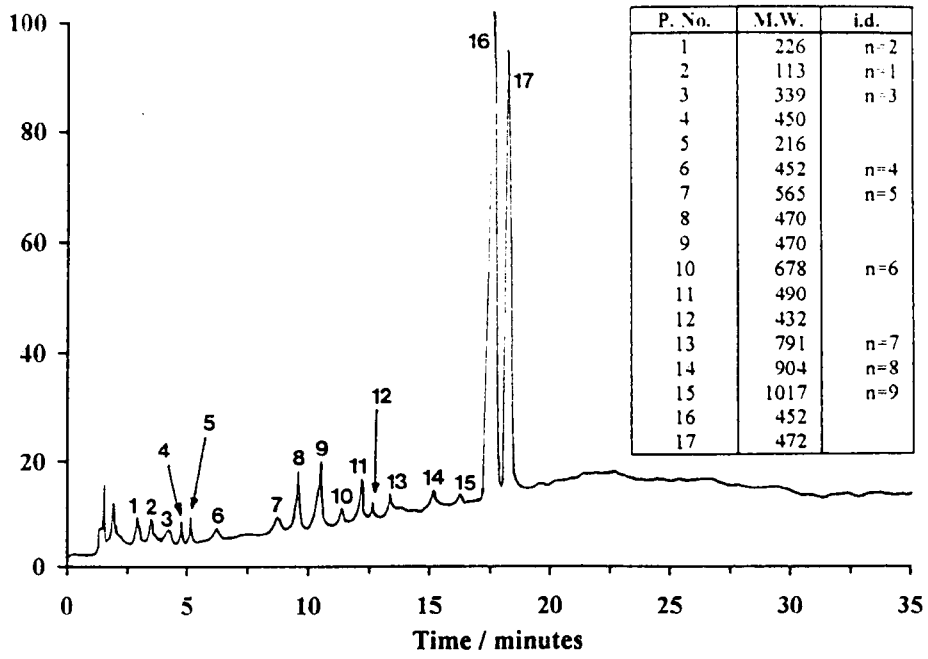


Figure 6.2 HPLC chromatogram of components migrating from aromatic based laminates into an aqueous food simulant, employing reverse phase chromatographic conditions (see Table 6.8)



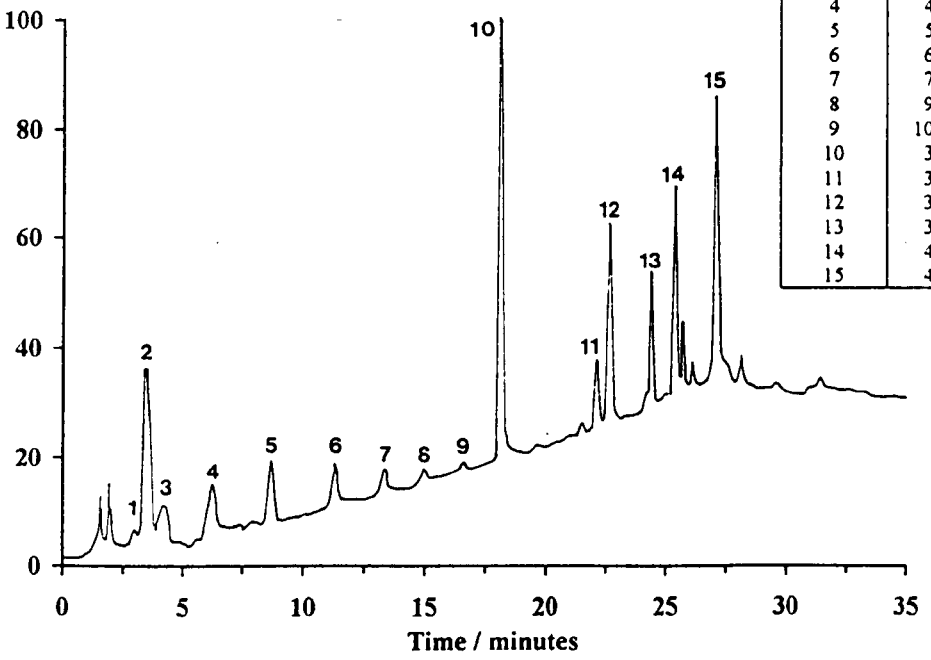
P. No.	M.W.	i.d.
1	226	n=2
2	113	n=1
3	339	n=3
4	452	n=4
5	565	n=5
6	678	n=6
7	791	n=7
8	904	n=8
9	1017	n=9
10	452	
11	472	
12	648	
13	668	
14	688	
15	708	
16	697	

Figure 6.3 Frit FAB LC-MS trace obtained from the aqueous extract from a chopped laminate containing a polyurethane adhesive incorporating an aromatic polyester.



P. No.	M.W.	i.d.
1	226	n=2
2	113	n=1
3	339	n=3
4	450	
5	216	
6	452	n=4
7	565	n=5
8	470	
9	470	
10	678	n=6
11	490	
12	432	
13	791	n=7
14	904	n=8
15	1017	n=9
16	452	
17	472	

Figure 6.4 **Frit FAB LC-MS trace obtained from the aqueous extract from the second chopped laminate containing a polyurethane adhesive incorporating an aromatic polyester.**



P. No.	M.W.	i.d.
1	226	n=2
2	113	n=1
3	339	n=3
4	452	n=4
5	565	n=5
6	678	n=6
7	791	n=7
8	904	n=8
9	1017	n=9
10	376	
11	390	
12	358	
13	394	
14	406	
15	498	

Figure 6.5 **Frit FAB LC-MS trace obtained from the aqueous extract from a chopped laminate containing a polyurethane adhesive incorporating an aliphatic polyether.**

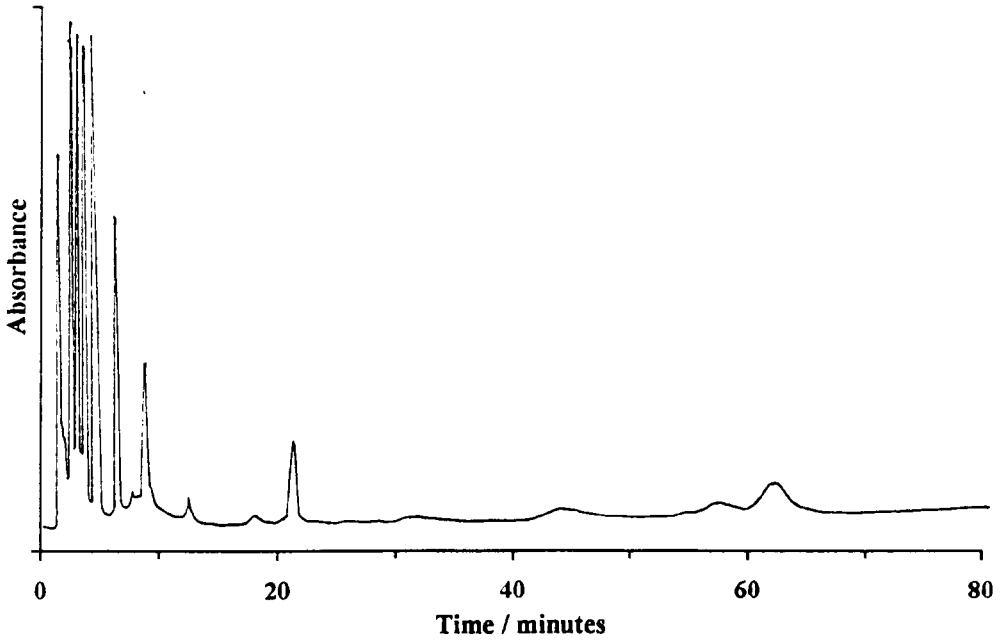


Figure 6.6 HPLC chromatogram of components migrating from a laminate formulated from a polyurethane adhesive containg an aliphatic polyether into an aqueous food simulant, employing reverse phase chromatographic conditions (see Table 6.8)

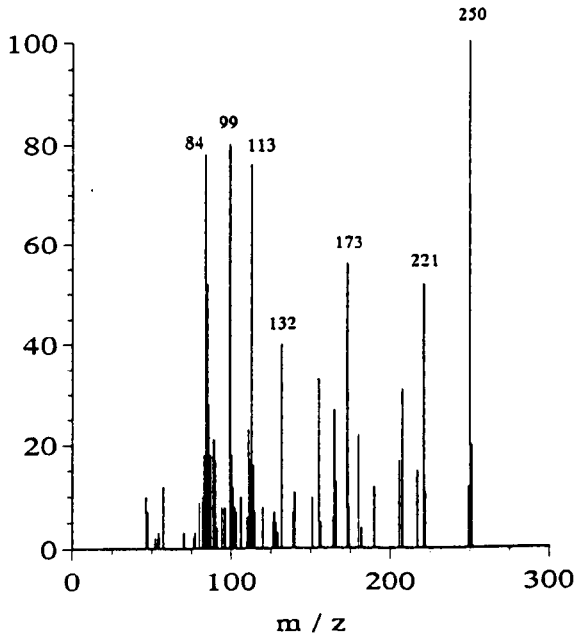


Figure 6.7 Mass spectral data obtained from the particle beam LC-MS analysis of aqueous extracts from aromatic adhesive based laminates. Indicating an identical mass spectra to that of MDI.

6.2.8 Quantification of polyester polyol material

Within the time available it was not possible to synthesise each of the individual components of the polyester resin in order to determine the appropriate UV response. It was therefore decided to determine the average relative response of these migrants to the response for ε-caprolactam. This approach would allow an estimate to be made of the level of polyester derived species in the aqueous food simulant.

Calibration solutions of polyester resin in acetonitrile were compared with similar solutions of ε-caprolactam also in acetonitrile. For equal concentrations of material, the relative absorbance units at 230nm were ε-caprolactam / polyester 1 : 18.5 which indicates a much better UV absorber in the polyester derived material, as anticipated. The level of polyester material migrating can therefore be estimated using the following equation :-

$$\text{Yield of polyester polyol } (\mu g\ dm^{-2}) = \frac{Y_{CAP} \times A_{POL}}{A_{CAP} \times 18.5}$$

Where :-

Y_{CAP} = Yield of ε-caprolactam ($\mu g\ dm^{-2}$)

A_{POL} = Total peak area of polyesters

A_{CAP} = Peak area of ε-caprolactam

From the data obtained in Table 6.10 it can be stated that the total amount of aromatic polyesters migrating from the laminates into an aqueous food simulant was quite low. As expected the levels found to be migrating from chopped laminates were larger than those for the corresponding pouches. This is a result of the adhesive layer being in direct contact with the aqueous food simulant when the laminates are chopped. In the pouch format, however, the polyesters have to migrate through the polyolefin film before entering the aqueous food simulant.

Sample	Migration / μg dm^{-2}	
	Chopped	Pouches
20μm NY66 / 50μm LLDPE *	100	30
70μm NY6 / 75μm LLDPE *	60	30
50μm NY6 / 50μm LLDPE *	140	40
15μm NY6 / 50μm LLDPE *	160	30

Results are subject to ± 20% variation

* = Side in contact with food simulant for single sided pouch tests.
NY6 = Nylon 6
NY66 = Nylon 6,6
LLDPE = Linear Low Density Polyethylene

Table 6.10 Estimation of amount of aromatic polyester migrating from aromatic adhesive based laminates into an aqueous food simulant.

6.3 SUMMARY

The LC-MS analyses confirmed the presence of ε-caprolactam and its cyclic oligomers up to the nonamer. Unreacted polyol materials from both aromatic and aliphatic based polyurethane adhesives were also found to migrate from the laminated film into an aqueous food simulant. In the absence of calibration data, the migration of polyol components cannot be directly quantified. However estimates based on the relative absorbances of ε-caprolactam and a polyester resin indicated levels of migration into an aqueous food simulants of between 60-160μg dm^{-2} for chopped laminate samples and 30-40μg dm^{-2} for pouch samples. No free diisocyanate species have been detected during the course of these particular HPLC investigations, but this would be expected with the presence of water in both the extraction procedure and the analysis. The situation regarding the presence of residual free diisocyanates within the laminate matrix is still unclear. The extraction procedure and the mobile phases used in the analysis should lead to the conversion of any residual diisocyanates to the corresponding diamine before it could be detected. It is interesting to note that both GC-MS and particle beam techniques, when used to study migrants into an aqueous simulant, have produced mass spectra identical to that of MDI. These results have been reproduced for

several different MDI based laminates. However, subsequent investigations by Lawson and Bird (270) have shown that MDI based compounds are thermally unstable under mass spectrometer ion source conditions and decompose to give MDI and its mass spectrum. The presence of such spectra do however indicate that MDI based species are found to migrate into the aqueous food simulant, to date there is no evidence for the structure or levels of this compound in the solution.

Many of the species identified as migrants in aqueous and oil simulants have been found in all the samples analysed. These include the antioxidants and their degradation products plus the nylon oligomers. No polyol derived species were found to migrate from the coextruded samples but all the laminates were found to posses them. Other compounds e.g. phenol and aniline have been detected in some but not all samples, and it is interesting to speculate on the origin of such variations. There are many factors which might affect these observations, ranging from different film thickness to the delay between fabrication of the laminate and the time of testing.

CHAPTER 7 : MISCELLANEOUS

7.1 INTRODUCTION

In this chapter experiments which do not fit easily under the headings of the previous four chapters are described. The use of silicone oil as an alternative to olive oil as a fatty food simulant was examined by analysing extracts from the oil by HPLC. HPLC techniques were also employed to compare the levels of migrants in aqueous extracts from pouches heated in an air oven and boiling water. Finally UV spectrophotometry was used to ascertain the levels of ε-caprolactam absorbed by dehydrated foods such as rice and spaghetti on boiling.

7.2 MATERIALS

Food Samples

Somerfield Spaghetti purchased at Gateways Foodmarket

Tilda American brown rice purchased at Gateways Foodmarket

Reagents

The following reagents were used:

Millipore water - (resistivity 18MΩ cm -milli-RO15 water system)

Napolina olive oil - purchased at retail outlet

Dow Corning 200/50 cs Silicone fluid
(BDH Laboratory Supplies, MERCK LTD, Lutterworth, Leicester, U.K.)

HPLC grade acetonitrile, and HPLC grade dichloromethane
(Rathburn, Walkerburn, U.K.)

Polyester Resin - (Holdens Surface Coating LTD. Birmingham, U.K.)

ε-Caprolactam 99+% [Gold label]

3,5-di-tert-butylphenol	**(3,5-DTBP)**
2,4-di-tert-butylphenol	**(2,4-DTBP)**
2,6-di-tert-butylphenol	**(2,6-DTBP)**
2,6-di-tert-butyl-1,4-benzoquinone	**(2,6-DTBBQ)**
2,6-di-tert-butyl-4-methylphenol	**(BHT)**
2,4,6-tri-tert-butylphenol	**(2,4,6-TTBP)**

(Aldrich Chemical Company, Gillingham, Dorset, U.K.)

The commercial antioxidants Irganox 1010, Irganox 1076, Irganox 1330 (1,3,5-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)-2,4,6-trimethylbenzene), Irgafos 168 and Irgafos P-EPQ were supplied by Ciba-Geigy Additives, Hulley road, Macclesfield, Cheshire, U.K.

7.3 ALTERNATIVE FATTY FOOD SIMULANTS

Due to the complex nature of most foods, the analytical task of determining what substances have migrated from the packaging is extremely difficult. To overcome this problem, food simulants are used in place of normal food. Overall migration experiments can be carried out reasonably readily using all of the four food simulants specified in directive 82/711/EEC (19). However, specific migration determinations require sophisticated analyses of the simulants in order to determine the levels of material migrating from the packaging into the simulant. Ideally, the simulant should be a pure and simple liquid, which will make the analytical migration testing as straight forward as possible, while ensuring that the liquid represents the respective classes of food.

For fatty foods the EC specified food simulants to use are rectified olive oil, sunflower oil or synthetic triglyceride HB 307 (19). However, difficulties in measuring the migration of many specific substances in these simulants has raised the need for alternatives. Alternative fatty food stimulants have been investigated including n-heptane (69), alcohol / water mixtures (274-275), and iso-octane (70, 276-277), but comparisons with EC specified fatty food simulants have confirmed that these alternative food simulants tend to grossly exaggerate the real migration values (275, 277).

Specific migration experiments using radiolabelled antioxidants with EC specified fatty food simulants have been conducted by several workers (278-281) on non commercial films. Obviously there is little chance of interference from the components in the oil with such studies, but the preparation of radioactive labelled examples of the species identified in this report plus their incorporation into real films would be impossible. In this investigation the suitability of silicone oil was investigated.

7.3.1 Olive oil Vs silicone oil extraction

As can be seen in Figure 7.1a HPLC analysis of acetonitrile extracts from olive oil using conditions appropriate for non-polar analytes (Table 6.5) produced a chromatogram which indicated the presence of significant levels of extractable material. Even after multiple extractions with acetonitrile the background level from the olive oil was still greater than the signal for migrating species from the plastic film.

As an alternative a Dow Corning silicone oil with a viscosity comparable to commercial olive oil was investigated. 50cm^3 of the silicone oil was solvent extracted with two 25cm^3 aliquots of acetonitrile, and analysed using the conditions cited in Table 6.5 for non-polar analytes. As can be seen in Figure 7.1b the principal attribute of this material is that it produces no detectable signal under the chromatographic conditions employed. It was therefore an ideal simulant to use for the quantitative analysis of migrants from films.

7.3.2 Quantification of antioxidants and their degradation products migrating from polyolefins into silicone oil

Before quantitative data for the levels of antioxidants and their degradation products migrating from polyolefin films into silicone oil could be determined the recovery efficiency for these compounds from silicone oil had to be ascertained.

Recovery Efficiency for Non-Polar Analytes

A dilute standard solution was prepared containing Irganox 1010, Irganox 1330, Irgafos 168, Irganox 1076 and TDTBPP dissolved in dichloromethane. 2cm^3 of this standard solution was added to 50cm^3 of silicone oil and the dichloromethane was allowed to evaporate off under normal ambient conditions for 30 minutes. After thorough mixing the silicone oil was extracted with two 25cm^3 aliquots of acetonitrile. These combined extracts were then pooled and analysed under the non-polar analyte conditions detailed in Table 6.5. This above

procedure was then repeated for a further two extractions to ascertain if all the non-polar analytes had been extracted from the silicone oil.

Recovery Efficiency for Polar Analytes

A dilute standard solution was prepared containing BHT, 3,5-DTBP, 2,4-DTBP, 2,6-DTBP, 2,6-DTBBQ, and 2,4,6-TTBP dissolved in dichloromethane. $2cm^3$ of this standard solution was added to $50cm^3$ of silicone oil and the dichloromethane was left to evaporate. After thorough mixing the silicone oil was extracted with two $25cm^3$ aliquots of acetonitrile. These combined extracts were then pooled and analysed under the polar analyte conditions cited in Table 6.5. The silicone oil was extracted a further two times using the protocol detailed above, and the extracts were then compared with the dilute standard solution.

The extraction efficiency results are tabulated in Table 7.1. As expected the more non-polar compounds required the greatest amount of extraction with acetonitrile. This information was then utilized to quantify the levels of these cited compounds migrating from polyolefin films into silicone oil.

Compound	% Extraction		
	1st Extract	2nd Extract	3rd Extract
3,5-DTBP	97	3	-
2,4-DTBP	96	4	-
2,6-DTBP	88	10	1
2,6 DTBBQ	85	12	2
BHT	80	16	2
2,4,6-TTBP	70	20	8
Irganox 1010	99	-	-
Irganox 1330	97	3	-
DTBPP	60	30	8
Irganox 1076	49	27	10
Irgafos 168	25	17	12

Results are subject to a ± 5% variation

Table 7.1 Extraction efficiency of non-polar and polar analytes from silicone oil

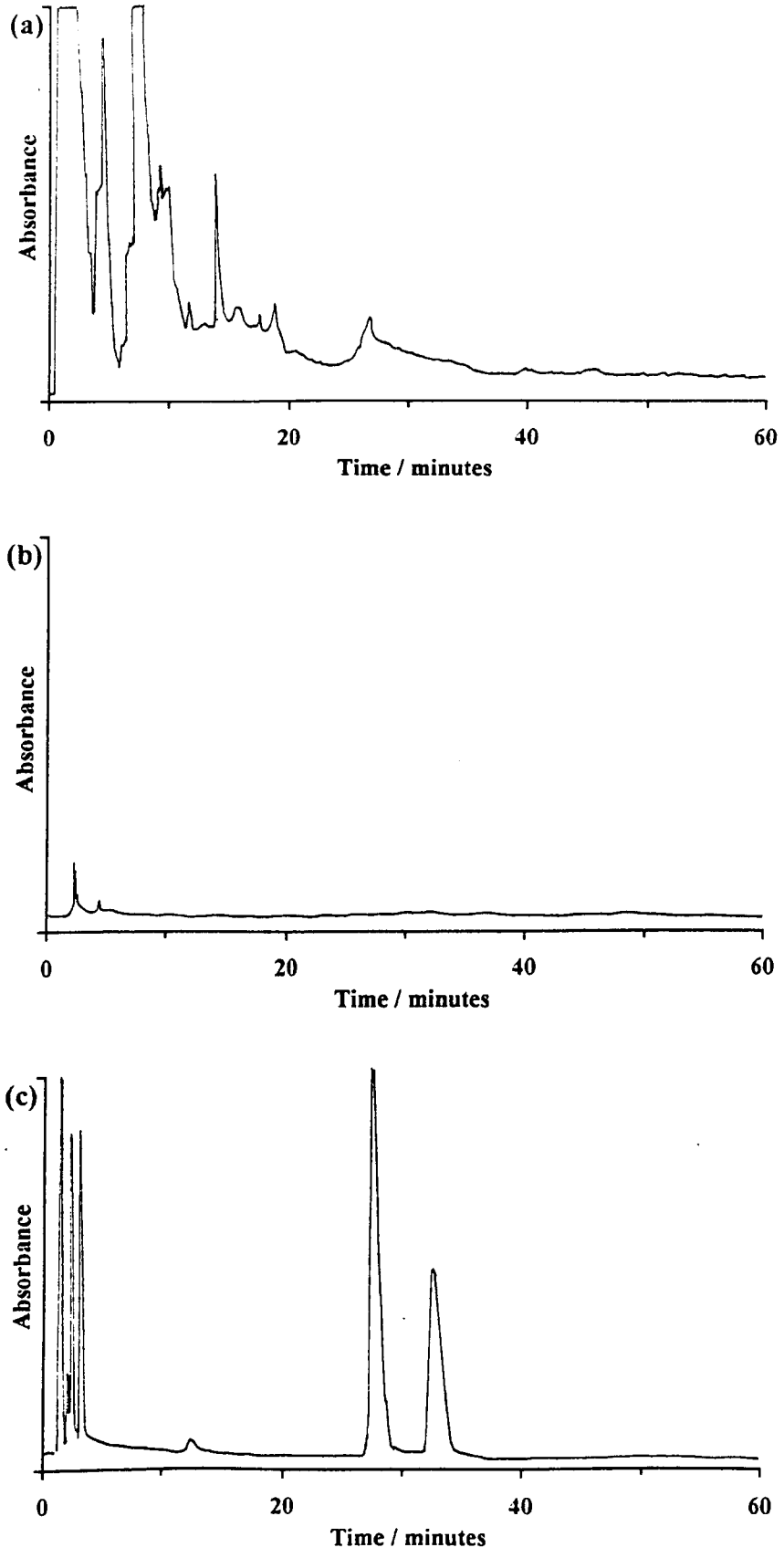


Figure 7.1 **HPLC analyses of an acetonitrile extract of blank olive oil prior to a migration experiment (a) and the extract from silicone oil both before (b) and after (c) a migration experiment**

7.3.2.1 Analysis of chopped and pouch film samples

Chopped Film Samples

Internal standards of Irganox 1330 for non-polar analytes and 2,4,6-TTBP for polar analytes were prepared in dichloromethane. To a round bottomed flask containing 50cm^3 of silicone oil 2cm^3 of the appropriate internal standard was added. After thorough mixing the flask was placed in air oven set to 100°C for 30 minutes to enable the oil to reach a temperature of 100°C. Film samples of 20 × 10cm were chopped into 1cm squares and placed in the round bottomed flask with the hot silicone oil. The flask was then heated in a water bath at 100°C for one hour. After this period of time the oil was decanted off from the residual film prior to extraction with two 25cm^3 aliquots of acetonitrile. These extracts were then pooled and analysed using the appropriate methodology as detailed in Table 6.5.

Pouch Samples

The silicone oil plus internal standard was prepared as detailed above for chopped films. The hot oil was then transferred to pouches with a known internal surface area. The pouches were then sealed with a Hulme Martin sealer and immersed in boiling water for one hour. The contents of the pouch were then extracted with two 25cm^3 aliquots of acetonitrile prior to HPLC analysis using the conditions cited in Table 6.5.

Figure 7.1c shows a typical chromatogram obtained from the analysis of non-polar antioxidants migrating from a chopped polyolefin film into silicone oil using the methodology detailed above.

7.3.3 Quantification of polyester polyol material migrating into fatty food simulants

HPLC analysis employing reverse phase conditions (Table 6.8) has indicated the presence of a range of aromatic polyesters migrating into an aqueous food simulant from the polyurethane adhesive used in certain boil in the bag films. However in order to determine how much polyester was migrating from the same film into a fatty food simulant, the fatty food simulant had to be extracted with a suitable solvent. The previous Section 7.3.2 employed acetonitrile to extract non polar and polar analytes from silicone oil. However, if this solvent was used all the antioxidants and their degradation products would be removed from the oil as well. In order to tailor the analysis to the chromatographic conditions (Table 6.8) the oil simulant was

extracted with millipore water. A comparison between a commercial sample of olive oil and silicone oil was then undertaken to determine the degree of migration of aromatic polyesters from the adhesive into the two fatty food simulants. Standard solutions of the polyester resin supplied by Holdens Surface Coatings LTD, Birmingham, were prepared in both oil samples in order to determine the levels of recovery from each oil prior to the migration determinations. In each case $50cm^3$ of the spiked oil was extracted with two $50cm^3$ aliquots of millipore water, and the resulting peak areas obtained using the reverse phase conditions compared with the peak area from the polyester resin standard solution. A similar recovery data for both oils was obtained of approximately 70%.

Both oil samples were then placed in contact with a chopped commercial 15μm NY6 / 50μm LLDPE laminate, containing aromatic polyester polyols in the adhesive. The chopped film was then heated for one hour at 100°C prior to decanting the oil of from the film. The $50cm^3$ of oil was then extracted with two $50cm^3$ aliquots of millipore water. These extracts were then pooled together and rotary evaporated under vacuum at a temperature of 50°C down to volume of approximately $6cm^3$. This solution was then made up to volume in a $10cm^3$ volumetric flask using an 80:20 methanol / water mixture prior to analysis by HPLC using the reverse phase conditions cited in Table 6.8. Using the methodology detailed in Section 6.2.8 it was possible to quantify the amount of polyester polyol material migrating from the laminate into the fatty food simulants by comparison with the peak area of a standard of ε-caprolactam. On the basis of these experiments 136μg dm^{-2} of polyester was found to migrate into olive oil and 188μg dm^{-2} into silicone oil from the chopped laminate after heating for one hour at 100°C. These results are subject to an error of ± 20% and whilst they demonstrate a greater migration into silicone oil the easy subsequent analysis of the migrants outweighs this concern.

7.4 EFFECTS OF COOKING METHOD ON EXTENT OF MIGRATION

Several of the meals sold in laminates of the type normally associated with boil in the bag systems are also cited by the manufacturer, as being suitable for microwave heating. Migration into the interior of the pouch, particularly of components from the nylon, may therefore be different since there is no external water to plasticize the nylon or to act as a preferential sink particularly for the caprolactam.

For these experiments pouches of dimensions 21 × 11cm were prepared and heat

sealed with a Hulme Martin sealer to give an internal surface area of $4dm^2$. Each pouch was then filled with $200cm^3$ of millipore water prior to sealing the water in the pouch. The pouches were then either placed in an air heated oven at 100°C for one hour or into boiling water for a similar period of time. These pouches were prepared from a 15μm NY6 / 50μm LLDPE commercial laminate film known to contain aromatic polyester polyols and an aromatic isocyanate. Comparisons were also made with commercially prepared pouches constructed from coextruded films 70μm NY6 / 70μm LLDPE.

After one hour at 100°C the aqueous extract was rotary evaporated under vacuum at a temperature of 70°C to a volume of approximately $6cm^3$. This solution was then made up to a final volume of $10cm^3$ using methanol / water 80 : 20 prior to analysis by HPLC using the reverse phase conditions cited in Table 6.8.

The results from this analysis are represented in Table 7.2. As can be seen from the data obtained the heating method used was found to effect the levels of ε-caprolactam migrating. Significantly more ε-caprolactam was found to migrate when the pouch was heated in an air oven. Inferring that the ε-caprolactam has migrated through the adhesive and polyolefin layers into the food simulant. No larger oligomers than the monomer of nylon were found to migrate, probably due to their increased size. Comparisons made between pouches constructed from a laminate and a coextruded film indicated that less ε-caprolactam migrated into the aqueous food simulant inside the pouch constructed from a coextruded film. The increased thickness of the polyolefin layer and the fact that a tie layer was used to bind the polyolefin to the polyamide was considered to be the reason for the lower migration levels from the coextruded films

Compound	Migration / μg dm^{-2}	
	Air Heated	Water Heated
Laminate		
ε-Caprolactam	820 ± 150	164 ± 30
Phenol	16 ± 4	10 ± 3
Aniline	3 ± 0.5	2 ± 0.5
Coextruded		
ε-Caprolactam	34 ± 3	15 ± 4

Table 7.2 Migration into an aqueous simulant versus heating method for a pouch sample

7.5 QUANTIFICATION OF ε-CAPROLACTAM ABSORBED BY DRY FOODS ON BOILING

As previously determined in Section 4.2.3.2 a yield of between 1 - 1.5% w/w of ε-caprolactam and its oligomers was found to migrate from chopped nylon 6 films into boiling water after one hour. In boil in the bag applications where nylon films are used the food within the pouch is usually separated from the nylon by a polyolefin and adhesive barrier. Therefore, any material migrating from the nylon film would have to penetrate both the adhesive and polyolefin layer before entering the food. However, these results do become significant if part of the meal is cooked in the same water as that used to cook the pouch. The most common types of food cooked in the water surrounding boil in the bag products are dehydrated foods such as spaghetti and rice.

In order to quantitatively determine the amount of ε-caprolactam absorbed by a dry food sample when boiled in a standard ε-caprolactam solution the following preliminary investigation was undertaken employing UV spectrophotometry.

A known mass of dry food samples (50g) were placed in a round bottomed flask with 100 cm^3 of a standard solution of ε-caprolactam in 18MΩ water (10mg dm^{-3}). The food was boiled under reflux conditions for one hour and the aqueous phase was then removed for analysis.

Prior to UV analysis the aqueous solution was cooled and filtered. The instrumental parameters employed were as follows :-

INSTRUMENT	: Pye Unicam SP800 UV/VIS Spectrophotometer
CELL	: 40mm path length [Quartz]
SCAN RANGE	: 180-275nm
REFERENCE BEAM	: 18MΩ Millipore Water

The resulting spectra obtained were then compared with the original caprolactam standard solution which had undergone the same experimental procedures as detailed above for the samples. Suitable calibration graphs were constructed by preparing a range of standard solutions of caprolactam in 18MΩ millipore water which were then used to ascertain the amount of caprolactam absorbed by the dehydrated foods.

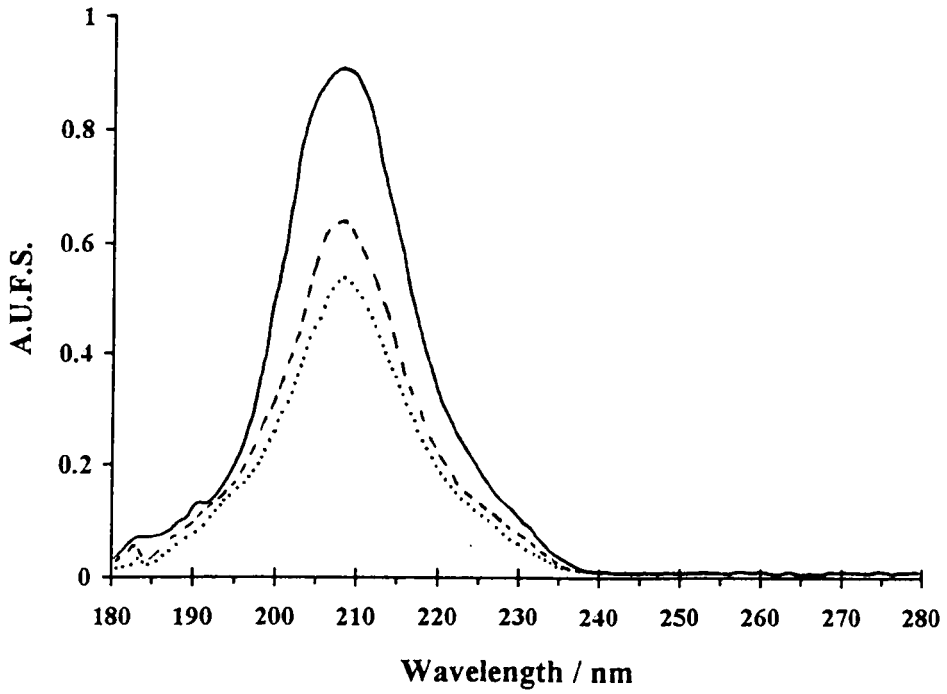
$$\text{Concentration of caprolactam absorbed by food} = \frac{(C_{STD} - C_{SPL}) \times 100}{C_{STD}}$$

Where :-

C_{STD} = Concentration (mg dm^{-3}) of caprolactam standard solution

C_{SPL} = Concentration (mg dm^{-3}) of caprolactam solution after boiling in contact with dehydrated food

On boiling samples of spaghetti and rice for one hour in a solution of caprolactam it can be seen (Figure 7.2) that the amount of caprolactam present in the aqueous media has fallen. Indicating that some of the caprolactam has been taken up by the food. Levels of caprolactam absorbed by the 50g of dry food were found to range from 30 ± 5% for brown rice to 40 ± 5% for spaghetti.



—— = Caprolactam standard solution

– – = Caprolactam standard solution on boiling with rice for one hour

· · · = Caprolactam standard solution on boiling with spaghetti for one hour

Figure 7.2 UV Spectra of caprolactam solutions

7.6 SUMMARY

HPLC analyses of extracts from silicone oil have indicated that it is a suitable alternative fatty food simulant to use for the determination of specific migrants from polymer films. Migration levels were found to be slightly higher when compared with olive oil, but in terms of consumer protection the identification of potential migrants outweighs these over estimates in the level of migration. It would therefore seam appropriate that the use of silicone oil in these and other elevated temperature applications be investigated further. Without an analytically viable alternative to olive oil it is difficult to see how meaningful specific migration data can be obtained without the use of radioactive tracers, which can not be readily used with commercial materials.

Differences in the levels of ε-caprolactam migrating from air and water heated pouches constructed from a laminate and a coextruded film were observed. A greater amount of ε-caprolactam was found to migrate into the aqueous food simulant inside the pouch when it was heated in an air oven. Therefore, the heating method was found to effect the levels of migrants.

The significant levels of oligomers found to be migrating from chopped nylon films directly into water (Chapter 4) are not representative of the amount expected to migrate into the food inside a commercial boil in the bag since the larger oligomers would have to migrate through the adhesive and polyolefin layers before entering the food. However, if part of the meal is cooked in the water surrounding the pouch then all of the oligomers extracted from the nylon by the water can potentially migrate into the food. Preliminary investigations carried out on dry foods boiled in a solution of caprolactam indicated that between 30 to 40% of the total amount of caprolactam available is removed by the typical amount of dry food (50g) supplied with some boil in the bag meals. This becomes particularly relevant when all the residual monomer in the nylon 6 film is extracted into the surrounding water after boiling for only 20 minutes, independent of whether a thick 80μm or thin 15μm film is used. The time period for complete extraction being similar to the cooking time of a boil in the bag meal.

CHAPTER 8 : CONCLUSIONS AND FURTHER WORK

8.1 CONCLUSIONS

The principal material employed in plastic vacuum flasks and kettles was found to be polypropylene. Investigations were carried out using both aqueous and fatty food simulants. The use of a fatty food simulant can be justified in the case of a flask where soups and even chickens are kept warm. However, the use of a fatty food simulant for a kettle is not immediately obvious, but during this investigation kettles have been found to be utilized for the poaching of eggs and even for the cooking of soup.

This work has confirmed the presence of antioxidants and their degradation products migrating into aqueous and fatty food simulants from these utensils after one hours exposure at 100°C. Antioxidants and their degradation products found in aqueous food simulants include Irganox 1010 (0.6μg dm^{-2}), 3,5-DTBP (1.7μg dm^{-2}) and 2,4-DTBP (0.2μg dm^{-2}). However, the levels and the number of species migrating were found to increase when an oil simulant is used, due to its ability to penetrate the polymer matrix and modify the local environment. Under these conditions Irganox 1010 (18μg dm^{-2}), Irgafos 168 (54μg dm^{-2}), 3,5-DTBP (8.9μg dm^{-2}), 2,4-DTBP (3.6μg dm^{-2}), 2,4,6-TTBP (6μg dm^{-2}) and TDTBPP (200μg dm^{-2}) were found to migrate into the oil simulant from the polypropylene.

Both of these polypropylene utensils are repeat use items i.e. used more than once. For example a flask may be used every day and a kettle boiled several times in a day, but the aqueous contents of a kettle are rarely emptied after each boil. HPLC and UV analyses indicated that initially the majority of the migrants in the food simulant were antioxidant degradation products and other polymerization aids which are left on the surface of the polymer after manufacture. On repeated extraction with an aqueous food simulant these degradation products and other aids to polymerization were removed and the initial levels of antioxidant Irganox 1010 increased from 0.6 to 3μg dm^{-2}. After five one hour exposures to boiling water the levels of migrants plateaux out as the amount of antioxidants and their degradation products blooming at the surface of the polypropylene reach an equilibrium.

Analyses carried out on films used for boil in the bag food packaging has confirmed the presence of a range of migrants from the films into both aqueous and oil simulants. The principal material in contact with the food in these applications is polyethylene. Low levels of

Irganox 1010 (<0.1 - 0.7μg dm^{-2}), 3,5-DTBP (0.1-0.2μg dm^{-2}) and 2,4-DTBP (<0.1μg dm^{-2}) were detected in aqueous food simulants in contact with the polyethylene film for one hour at 100°C. Again the quantities and number of antioxidants and their degradation products migrating from the polyethylene were found to increase when an oil simulant was used. Antioxidants, Irganox 1010 (5.0 - 45μg dm^{-2}) and Irgafos 168 (10 - 44μg dm^{-2}) were found to migrate into oil simulants after one hour at 100°C, in addition, antioxidant degradation products, 3,5-DTBP (3 - 4μg dm^{-2}), 2,4-DTBP (3 - 12.2μg dm^{-2}), 2,4,6-TTBP (3.8-5.8μg dm^{-2}) and TDTBPP (8.1-16.3μg dm^{-2}) were also found to migrate. However, the morphology and thickness of the polyethylene appeared to play a significant part in the amount of material migrating. Under comparable conditions, and using the same thickness of polyethylene more residual antioxidants and degradation products were found to migrate from films constructed from LLDPE than HDPE. Thicker polyethylene films constructed from the same material were also found to lead to increased levels of migrants due to a greater mass of film being extracted.

HPLC and LC-MS analyses of migrants from the nylon layer of the laminate has confirmed the presence of ε-caprolactam and its cyclic oligomers (up to the nonamer) in water boiled in direct contact with the food grade nylon 6. As expected thicker nylon 6 films produced a greater mass of migrants and required longer extraction times (up to 4 hours for the removal of larger cyclic oligomers from an 80μm film). Levels of residual monomer migrating after one hours exposure to water boiled in direct contact with the nylon ranged from 0.2 to 1mg dm^{-2}, which exceeds the specific migration limit stipulated by the EC for ε-caprolactam of 15mg kg. In addition, levels of oligomers were found to range from 1.2 to 3.1mg dm^{-2}, but no specific migration limits have been specified for these migrants.

The significant levels of oligomers found to migrate from nylon films directly into water are not representative of the amount expected to migrate into the food inside a commercial boil in the bag since the larger oligomers would have to migrate through the adhesive and polyolefin layers before entering the food. Investigations have shown that the only material found to migrate through the packaging from the nylon layer into an aqueous food simulant after one hours boiling is ε-caprolactam, at levels ranging from 15- 164μg dm^{-2}. However, if part of the meal is cooked in the water surrounding the pouch then all of the oligomers extracted from the nylon by the water can potentially migrate into the food. Preliminary investigations carried out on dry foods boiled in contact with a standard solution

of ε-caprolactam have indicated that between 30 to 40% of the total amount of caprolactam available is removed by the typical amount of dry food (50g) supplied with boil in the bag meals.

LC-MS and HPLC techniques have also confirmed the presence of unreacted polyol materials migrating from both aromatic and aliphatic based polyurethane adhesives into aqueous food simulants. Estimates based on the relative absorbances of ε-caprolactam and a polyester resin have indicated levels of migration into an aqueous food simulant after one hour at 100°C of between 60 - 160μg dm^{-2} for chopped laminate samples and 30 - 40μg dm^{-2} for pouch samples. Any residual aromatic isocyanates present in the adhesive would be converted to the corresponding amine, and modified Marcali colourimetric analyses indicated levels of residual amines ranging from 0.1 to 1μg dm^{-2}.

8.2 FURTHER WORK

Boil in the bag foods are normally sold as two component sachets, one containing the meat and the other a dry food. This dry food (rice, spaghetti) is usually immersed in the same water as the pouch containing the meat sachet, therefore, any migrants that have entered the boiling water could be absorbed by the dry food. As previously determined a significant quantity of these migrants in the water are residual oligomers of nylon 6. Preliminary investigations using UV spectroscopy have indicated that the dry food when boiled in contact with a solution of ε-caprolactam does absorb some of the monomer of nylon. However, further work could be carried out to develop a method for determining how much of the migrating oligomers from the nylon part of the packaging are being absorbed by the dry food. This could be accomplished by a HPLC technique similar to that mentioned in Chapter 4. However, the aqueous sample prior to analysis would require some form of sample clean up procedure to remove the components in the aqueous medium which have come from the dry food. Once a suitable clean up technique has been developed this analysis could be extended to other migrants from the pouch.

HPLC and LC-MS investigations on the adhesives used in boil in the bag laminates have shown a range of species migrating into food simulants. The species migrating from aromatic polyurethane adhesives have been identified as residual oligomers from the polyols. However, further investigations with a commercial sample of aliphatic and polyether polyol

resins are necessary to identify the species migrating from laminates constructed from these forms of adhesive.

The identities of a range of polyester polyols migrating from the adhesive layer of laminates have been determined by LC-MS, but other than a preliminary investigation by UV spectroscopy, no experiments have been undertaken to quantify the levels of the individual polyesters migrating. In order to do this each of the individual polyester polyols identified would have to be synthesized. Standard solutions of each of these pure standards could then be injected onto the HPLC and the subsequent response used to determine the specific levels of each polyester polyol migrating from the adhesive into the food simulant.

In this investigation silicone oil was used as an alternative fatty food simulant to quantify the species migrating from the food contact polymer. However, further comparative studies with olive oil are necessary to confirm its suitability as a fatty food simulant. This is particularly difficult when comparisons are made of levels of specific migrants leaching out of plastics, due to the difficulties in analysing olive oil. In order to do a comparison radio-labelled species would have to be incorporated into the polymer and exposed to both food simulants under comparable conditions for the same period of time.

Finally colourimetric analyses carried out on migrants from the adhesive used in boil in the bag laminates are unable to differentiate between aniline, diphenylamine and MDA. It is also unable to detect aliphatic isocyanates migrating since these species do not produce a colour change on diazotization. In order to quantify these species migrating an analytical technique possibly employing HPLC would have to be developed. This is of particular importance due to the toxic nature of the species.

APPENDIX 1

Film and Laminate Dimensions

Sample	Measured Thickness /μm	Mass / gdm^{-2}
15μm LLDPE	15 - 20	0.17 ± 0.01
15μm LLDPE	18 - 20	0.17 ± 0.01
50μm LLDPE	45 - 50	0.43 ± 0.02
50μm LLDPE	48 - 52	0.47 ± 0.01
50μm LLDPE	50 - 60	0.47 ± 0.02
15μm HDPE	15 - 20	0.14 ± 0.01
15μm HDPE	10 - 25	0.11 ± 0.07
50μm HDPE	50 - 55	0.46 ± 0.01
15 μm NY	13 - 17	0.18 ± 0.01
20 μm NY (6,6)	18 - 22	0.22 ± 0.01
25.4μm NY	23 - 27	0.29 ± 0.01
50 μm NY	48 - 52	0.56 ± 0.01
80 μm NY	77 - 83	0.86 ± 0.02
15μm NY/50μm LLDPE	62 - 68	0.66 ± 0.01
70μm NY/75μm LLDPE	145 - 160	1.58 ± 0.02
20μm NY/50μm LLDPE (co)	69 - 75	0.70 ± 0.01
50μm NY/50μm LLDPE (co)	100 - 105	1.03 ± 0.02
100μm NY/75μm LLDPE	175 - 180	1.87 ± 0.02
50μm LLDPE/50μm LLDPE	102 - 106	0.99 ± 0.02

Note : LLDPE = Linear Low Density Polyethylene
HDPE = High Density Polyethylene
NY = Nylon 6
NY (6,6) = Nylon 6,6
(co) = Co-extruded film

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